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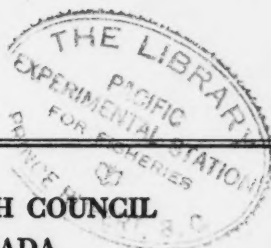
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# Canadian Journal of Research

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VOL. 16, SEC. A.

DECEMBER, 1938

NUMBER 12

## VIBRATIONS ON POWER LINES IN A STEADY WIND<sup>1</sup>

### V. RESONANCE OF STRINGS WITH STRENGTHENED ENDS

By R. RUEDY<sup>2</sup>

#### Abstract

The resonance frequencies, and in particular all the overtones of a string along which the linear density varies according to the law  $\rho(1 + \lambda x/L)^m$ , are slightly higher than the frequencies of a uniform string of the same total mass when the ratio between the mass of an element at the end and a corresponding element at the centre is varied between 1 and 25. In order to bring a string with strengthened ends into resonance it is necessary not only that the force acting on unit length of the string be of the same frequency as one of the resonance frequencies, and that its strength varies along the string in proportion to the amplitudes of the corresponding standing waves, but it must also be proportional to the mass of each element. It is therefore more difficult to produce true resonance in a string with strengthened ends than in a uniform string.

#### Comparison between the Frequencies of Strengthened and of Uniform Strings

On the assumption that the mass per unit length increases along a string according to the law  $\rho_0(1 \pm \lambda x/L)^m$ , where the lower sign applies to negative values of  $x$  on strings that are symmetrical with respect to the origin and of total length  $l = 2L$ , the frequencies corresponding to wave-shapes giving an odd number of loops follow from the equation

$$J_{\frac{m+1}{m+2}}\left(\frac{\pi/\lambda}{m+2} \frac{\nu}{\nu_0}\right) J_{\frac{1}{m+2}}\left(\frac{\pi/\lambda}{m+2} \frac{\nu}{\nu_0} (1+\lambda)^{\frac{m+2}{2}}\right) + J_{-\frac{m+1}{m+2}}\left(\frac{\pi/\lambda}{m+2} \frac{\nu}{\nu_0}\right) J_{-\frac{1}{m+2}}\left(\frac{\pi/\lambda}{m+2} \frac{\nu}{\nu_0} (1+\lambda)^{\frac{m+2}{2}}\right) = 0.$$

The frequency  $\nu_0$ , which appears in the independent variable, is the fundamental frequency  $(S/16\rho_0 L^2)^{\frac{1}{2}}$  of the uniform string of total length  $l$ ; in the treatment of the strengthened string this frequency is replaced by the smallest solution  $\nu_1$  of the equation just mentioned. The frequency of standing waves that have an odd number of loops is determined by the condition that a loop lies at the very centre of the string, whereas the ends remain motionless;

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for the vibrations that produce an even number of loops the ends and the centre are at rest, and the possible frequencies follow from the equation

$$J_{\frac{1}{m+2}}\left(\frac{\pi/\lambda}{m+2} \frac{\nu}{\nu_0}\right) J_{-\frac{1}{m+2}}\left(\frac{\pi/\lambda}{m+2} \frac{\nu}{\nu_0} (1+\lambda)^{\frac{m+2}{2}}\right) - J_{-\frac{1}{m+2}}\left(\frac{\pi/\lambda}{m+2} \frac{\nu}{\nu_0}\right) J_{\frac{1}{m+2}}\left(\frac{\pi/\lambda}{m+2} \frac{\nu}{\nu_0} (1+\lambda)^{\frac{m+2}{2}}\right) = 0.$$

The approximate ratios  $\nu/\nu_0$  between the allowed frequencies of the strengthened string and the fundamental frequency  $\nu_0$  of the uniform string are given in Table I for two degrees of strengthening, namely for  $(1 + \lambda)^m = 4$  and  $(1 + \lambda)^m = 16$ .

TABLE I

COMPARISON BETWEEN THE FREQUENCIES  $\nu$  OF STRINGS WITH STRENGTHENED ENDS AND THE LOWEST FREQUENCY  $\nu_0$  OF THE CORRESPONDING UNIFORM STRING.

	$(1 + \lambda)^m = 4$			$(1 + \lambda)^m = 16$		
	$m = 1$ $\lambda = 3$	$m = 2$ $\lambda = 1$	$m = 6$ $\lambda = 0.26$	$m = 1$ $\lambda = 15$	$m = 2$ $\lambda = 3$	$m = 6$ $\lambda = 0.587$
$\nu_1/\nu_0$	0.74	0.75	0.76		0.48	
$\nu_2/\nu_0$	1.21	1.30	1.39		0.76	
$\nu_3/\nu_0$	1.98	2.00	2.00	1.20	1.30	
$\nu_4/\nu_0$	2.59	2.67	2.74	1.55	1.60	1.64
$\nu_5/\nu_0$	3.18	3.3	3.4	1.92	2.00	2.05
$\nu_6/\nu_0$	3.87	4.0	4.1	2.25	2.44	2.66
$\frac{\pi}{\lambda(m+2)}$	0.35	0.785	1.51	0.07	0.26	0.66

The natural frequencies of the string for which  $(1 + \lambda)^m = 4$  are about 5/3 times as large as those for  $(1 + \lambda)^m = 16$ , and about twice as large as the frequencies of the string for which the degree of strengthening is 25.

With the exception of the first few harmonics, the natural frequencies of the uniform string of unit mass  $\rho_0$  are  $1/\gamma$  times as large as the corresponding resonance frequencies of the string along which the mass of unit length increases from the value  $\rho_0$  at the centre to the value  $\rho_0 Q$  at the ends. The reduction factor

$$\gamma = \frac{m+2}{2} \frac{\lambda}{(1+\lambda)^{\frac{m+2}{2}} - 1} = \frac{Q^{\frac{1}{2m}} - 1}{Q^{\frac{m+2}{2m}} - 1} \frac{m+2}{2}$$

is constant for given values of  $Q$  and  $m$ . In other words, as far as the higher frequencies are concerned, the string behaves as though it had a uniform linear density equal to  $\rho_0/\gamma^2$  grams per unit length, and the successive overtones are therefore separated by constant intervals. It is useful to examine in this connection whether the values  $\rho_0/\gamma^2$  of the density are higher or lower than the average density of the strengthened string, that is, to determine how

much the same amount of material reduces the frequencies of vibration when it is concentrated near the ends instead of being uniformly distributed.

If the ratio between the mass of unit length at the end and the corresponding mass at the centre is

$$Q = (1 + \lambda)^m,$$

which corresponds to the assumed increase in mass along the string according to the law  $\rho_0(1 + \lambda x/L)^m$ , the average mass per unit length is

$$\rho = \frac{\rho_0}{L} \int_0^L (1 + \lambda x/L)^m dx = \frac{(1 + \lambda)^{m+1} - 1}{\lambda(m+1)} \rho_0 = \frac{Q^{\frac{m+1}{m}} - 1}{(m+1)(Q^{\frac{1}{m}} - 1)} \rho_0$$

Thus a linear increase in density gives of course an average density equal to  $\rho_0(1 + Q)/2$  or  $2.5\rho_0$  for  $Q = 4$  and  $13\rho_0$  for  $Q = 25$ , whereas the values of  $\rho_0/\gamma^2$  are 2.5 and 11.5, respectively. The higher frequencies remain, therefore, about the same whether the distribution be linear or uniform, providing only that the total mass of the string remains constant.

The same conclusion holds for all the distributions of the type  $\rho_0(1 + \lambda x/L)^m$ , regardless of the value for  $m$ . When, in particular, after a certain ratio  $Q$  has been chosen, successively larger values are given to  $m$ , decreasing values result for  $\lambda$ , since  $(1 + \lambda)^m = Q$  or  $\lambda = Q^{\frac{1}{m}} - 1$ . At the limit

$$\rho = \frac{(1 + \lambda)^{m+1} - 1}{\lambda(m+1)} \rho_0 = \frac{Q^{\frac{m+1}{m}} - 1}{(Q^{\frac{1}{m}} - 1)(m+1)} \rho_0 = \frac{Q - 1}{\ln Q} \rho_0 \text{ for } m = \infty.$$

The limit of the fraction is 2.16 for  $Q = 4$ , and 7.46 for  $Q = 25$ , in place of the averages 2.5 and 13 for the linear increase in density. The limit of  $\gamma$ , on the other hand, for the standing waves with an even number of loops, is

$$\gamma = \frac{2(\sqrt{Q} - 1)}{\ln Q} \text{ for } m = \infty$$

that is

$$\begin{aligned} \gamma_{\infty} &= 1.44 \text{ for } Q = 4 \\ \gamma_{\infty} &= 2.48 \text{ for } Q = 25, \end{aligned}$$

and a uniform string giving, above the second or third overtone, the same resonance frequencies as the string with strengthened ends would, therefore, have to possess a mass equal to  $2.07\rho_0$  per unit length for a ratio  $Q$  equal to 4, and a uniform mass  $6.15\rho_0$  per unit length for  $Q = 25$ , values that do not differ greatly from the average mass of the non-uniform string. As regards the reduction in the frequency of the resonance vibration, it is most pronounced for the uniform distribution of the mass.

In order to complete the comparison between the behavior of strengthened and of uniform strings it is necessary to study also the amplitudes produced by an external force along the string with strengthened ends. Before this problem is dealt with, however, the solution obtained when  $m$  tends to infinity is

worthy of a brief treatment from a different viewpoint. At the limiting value of  $m$  the use of the Bessel functions  $J_{1/\mu}$  and  $J_{-1/\mu}$  ceases to give two independent solutions, so that  $J_{-1/\mu}$  must be replaced, for instance, by Weber's function:

$$Y_0(\beta\xi) = \frac{2}{\pi} \left( \ln \frac{\beta\xi}{2} + \gamma \right) J_0(\beta\xi) - \frac{2}{\pi} \sum_{r=1}^{\infty} (-1)^r \frac{(\beta\xi/2)^{2r}}{(r!)^2} \left( 1 + \frac{1}{2} + \frac{1}{3} \cdots \frac{1}{r} \right),$$

where  $\gamma = 0.5772$  is Euler's constant.

At the same time the variable is

$$\frac{\pi}{\lambda(m+2)} (1 + \lambda x/L)^{\frac{m+2}{2}} = \frac{\pi}{\ln Q} Q^{\xi/2} \quad (\text{for } m = \infty)$$

and the frequency equation becomes

$$J_0 \left( \frac{\pi}{\ln Q} \frac{\nu}{\nu_0} \right) Y_0 \left( \frac{\pi}{\ln Q} \frac{\nu}{\nu_0} \sqrt{Q} \right) = J_0 \left( \frac{\pi}{\ln Q} \frac{\nu}{\nu_0} \sqrt{Q} \right) Y_0 \left( \frac{\pi}{\ln Q} \frac{\nu}{\nu_0} \right).$$

Hence for large values of  $m$  the resonance frequencies of the strengthened string are determined by the same equation that gives the natural frequencies of vibration of a stretched annular membrane clamped between an outer circle of radius 1 and an inner circle of radius  $(1 + \lambda)^{(m+2)/2} = Q^{\frac{1}{2}}$ . This equation is considered in detail in the theory of loud-speakers. The higher overtones obey the equation

$$\begin{aligned} J_0(\beta b) Y_0(\beta a) - J_0(\beta a) Y_0(\beta b) &= \sin \left( \beta a - \frac{\pi}{4} \right) \cos \left( \beta b - \frac{\pi}{4} \right) \\ &- \sin \left( \beta b - \frac{\pi}{4} \right) \cos \left( \beta a - \frac{\pi}{4} \right) = \sin \beta(a-b) \end{aligned}$$

so that

$$\frac{\nu}{\nu_0} = n \frac{\ln Q}{1 - \sqrt{Q}}.$$

This result confirms the conclusion that the higher overtones are separated by equal frequency intervals.

### Forced Vibrations of the String with Strengthened Ends in the Absence of Damping

The equation of motion of a string set into vibration by an alternating force  $F(x) \cos 2\pi\nu t$  or  $F(x)e^{-i\omega t}$  dynes per cm. and opposed by  $R \partial y / \partial t$ , a frictional force assumed to be proportional to the velocity but virtually independent of the frequency, is

$$\begin{aligned} m(x) \frac{\partial^2 y}{\partial t^2} &= S \frac{\partial^2 y}{\partial x^2} + F(x) e^{-i2\pi\nu t} - R \frac{\partial y}{\partial t} \\ \frac{\partial^2 y}{\partial t^2} &= \frac{S}{m(x)} \frac{\partial^2 y}{\partial x^2} + \frac{F(x)}{m(x)} e^{-i2\pi\nu t} - \frac{R}{m(x)} \frac{\partial y}{\partial t}. \end{aligned}$$

On the assumption that a solution exists such that

$$y = Y(x)T(t)$$

and that, apart from a possible lag, the time function  $T(t)$  is the same for the forced motion and the external force, the equation

$$-\omega^2 Y = \frac{S}{m(x)} \frac{d^2 Y}{dx^2} + \frac{F(x)}{m(x)} - i\omega \frac{R}{m(x)} Y$$

or

$$\frac{d^2 Y}{dx^2} + \frac{\omega^2}{S} m(x) Y = -\frac{F(x)}{S} - i\omega \frac{R}{S} Y$$

is obtained for the relation between the variables  $Y$  and  $x$ . When distances and displacements are expressed as fractions of the length  $L$  of the string on one side of the origin, putting  $\eta = y/L$  and  $\xi = 1 + \lambda x/L$

$$m(x) = \rho(\xi) = \rho_0(1 + \lambda x/L)^m = \rho_0 \xi^m,$$

the shape of the string is at any given moment determined by

$$\frac{d^2 \eta}{d\xi^2} + \frac{\omega^2}{4\lambda^2 \nu_0^2} \xi^m \eta = -\frac{LF(\xi)}{S\lambda^2} - \frac{i\omega R}{\lambda^2 S} L^2 \eta.$$

In the absence of the terms on the right-hand side, the solution of the equation yields the undamped free motion of the string:

$$\eta = C_1 \sqrt{\xi} J_{\frac{1}{m+2}} \left( \frac{\pi/\lambda}{m+2} \frac{\nu}{\nu_0} \xi^{\frac{m+2}{2}} \right) + C_2 \sqrt{\xi} J_{-\frac{1}{m+2}} \left( \frac{\pi/\lambda}{m+2} \frac{\nu}{\nu_0} \xi^{\frac{m+2}{2}} \right).$$

If the solution

$$\eta = C_1 y_1 + C_2 y_2$$

of the reduced equation, called the complementary function for the complete equation, is known, the general solution of the complete equation may always be obtained in terms of quadratures by assuming  $F$ ,  $C_1$ , and  $C_2$  to be functions of  $\xi$  and applying Lagrange's method of the variation of the constants of integration. For a differential equation of the second order with second member  $P(\xi) = -LF(\xi)/S\lambda^2$ , the general solution is

$$\eta = c_1 y_1 + c_2 y_2 - y_1 \int \frac{y_2 P(\xi)}{y_1 y_2' - y_2 y_1'} + y_2 \int \frac{y_1 P(\xi)}{y_1 y_2' - y_2 y_1'}$$

or

$$\eta = c_1 y_1 + c_2 y_2 - y_1 C_1(\xi) + y_2 C_2(\xi).$$

When

$$y_1 = \sqrt{\xi} J_{\frac{1}{\mu}} \left( \frac{\pi/\lambda}{m+2} \frac{\nu}{\nu_0} \xi^{\frac{m+2}{2}} \right) = \sqrt{\xi} J_{\frac{1}{\mu}} (\beta \xi^{\frac{m+2}{2}})$$

$$y_2 = \sqrt{\xi} J_{-\frac{1}{\mu}} \left( \frac{\pi/\lambda}{m+2} \frac{\nu}{\nu_0} \xi^{\frac{m+2}{2}} \right) = \sqrt{\xi} J_{-\frac{1}{\mu}} (\beta \xi^{\frac{m+2}{2}})$$

then

$$y_1 y_2' - y_2 y_1' = -\frac{\sin \pi/\mu}{\pi/\mu}.$$

The integrals for  $C_1$  and  $C_2$  can be evaluated when  $P(\xi)$  is represented by certain simple functions. From experiments with ordinary strings it is known that in order to produce full resonance the applied force has to agree not only in frequency with one of the natural frequencies of vibration of the string, but it must also vary in strength along the string according to the relation expressing the amplitudes of the stationary waves on the string, so that it is always in phase with the motion. However, with these assumptions the amplitudes become infinite, and the solution is without great practical interest. A different law will be considered for the force that acts upon the strengthened string, namely

$$\frac{F(\xi)}{\xi^m} = A^+ J_{\frac{1}{\mu}} \left( \frac{\pi/\lambda}{m+2} \frac{\nu}{\nu_0} \xi^{\frac{m+2}{2}} \right) + A' J_{-\frac{1}{\mu}} \left( \frac{\pi/\lambda}{m+2} \frac{\nu}{\nu_0} \xi^{\frac{m+2}{2}} \right),$$

where  $\nu$ , the frequency of the external force, may have any value but is supposed to differ, even if only slightly, from the frequency  $\nu_n$  corresponding to a standing wave. The amplitudes  $A^+$  and  $A'$  have the dimensions  $MT^{-2}$  of a force referred to unit length.

By a change in the variable to  $z = \xi^{\frac{m+2}{2}}$  the well known formulas for the integral of a product of two Bessel functions become

$$\begin{aligned} \frac{m+2}{2} (\alpha^2 - \beta^2) \int \xi^{m+1} J_{\frac{1}{\mu}} \left( \alpha \xi^{\frac{m+2}{2}} \right) J_{-\frac{1}{\mu}} \left( \beta \xi^{\frac{m+2}{2}} \right) d\xi \\ = \frac{2}{\mu} J_{\frac{1}{\mu}} \left( \alpha \xi^{\frac{m+2}{2}} \right) J_{-\frac{1}{\mu}} \left( \beta \xi^{\frac{m+2}{2}} \right) + \beta \xi^{\frac{m+2}{2}} J_{\frac{1}{\mu}} \left( \alpha \xi^{\frac{m+2}{2}} \right) J_{-\frac{1}{\mu}-1} \left( \beta \xi^{\frac{m+2}{2}} \right) \\ - \alpha \xi^{\frac{m+2}{2}} J_{\frac{1}{\mu}-1} \left( \alpha \xi^{\frac{m+2}{2}} \right) J_{-\frac{1}{\mu}} \left( \beta \xi^{\frac{m+2}{2}} \right) \\ \frac{m+2}{2} (\alpha^2 - \beta^2) \int \xi^{m+1} J_{\frac{1}{\mu}} \left( \alpha \xi^{\frac{m+2}{2}} \right) J_{\frac{1}{\mu}} \left( \beta \xi^{\frac{m+2}{2}} \right) d\xi \\ = \xi^{\frac{m+2}{2}} \left( \beta J_{\frac{1}{\mu}} \left( \alpha \xi^{\frac{m+2}{2}} \right) J_{\frac{1}{\mu}-1} \left( \beta \xi^{\frac{m+2}{2}} \right) - \alpha J_{\frac{1}{\mu}-1} \left( \alpha \xi^{\frac{m+2}{2}} \right) J_{\frac{1}{\mu}} \left( \beta \xi^{\frac{m+2}{2}} \right) \right) \\ = \xi^{\frac{m+2}{2}} \left( \alpha J_{\frac{1}{\mu}+1} \left( \alpha \xi^{\frac{m+2}{2}} \right) J_{\frac{1}{\mu}} \left( \beta \xi^{\frac{m+2}{2}} \right) - \beta J_{\frac{1}{\mu}} \left( \alpha \xi^{\frac{m+2}{2}} \right) J_{\frac{1}{\mu}+1} \left( \beta \xi^{\frac{m+2}{2}} \right) \right) \end{aligned}$$

for any two Bessel functions, where

$$\alpha^2 = \frac{4L^2\pi^2/\lambda^2}{(m+2)^2} \nu^2 \frac{\rho_0}{S}, \quad \beta^2 = \frac{4L^2\pi^2/\lambda^2}{(m+2)^2} \nu_n^2 \frac{\rho_0}{S}$$

The factor  $\alpha$  refers to the external force, the factor  $\beta$  to the resonance frequencies of a string of arbitrary length.

With  $\mu = m + 2$  the final solution, valid when  $\nu$  differs from  $\nu_n$ , or  $\alpha$  differs from  $\beta$ , is

$$\eta = c_1 y_1 + c_2 y_2 + \frac{4L}{(m+2)^2 (\alpha^2 - \beta^2)} \left( A^+ \sqrt{\xi} J_{\frac{1}{m+2}} \left( \alpha \xi^{\frac{m+2}{2}} \right) + A' \sqrt{\xi} J_{-\frac{1}{m+2}} \left( \alpha \xi^{\frac{m+2}{2}} \right) \right)$$

or

$$\frac{\eta}{\sqrt{\xi}} = c_1 J_{\frac{1}{m+2}}(\beta \xi^{\frac{m+2}{2}}) + c_2 J_{-\frac{1}{m+2}}(\beta \xi^{\frac{m+2}{2}}) + \frac{1}{\rho_0 \pi^2 L (\nu^2 - \nu_n^2)} \left( A^+ J_{\frac{1}{m+2}}(\alpha \xi^{\frac{m+2}{2}}) + A' J_{-\frac{1}{m+2}}(\alpha \xi^{\frac{m+2}{2}}) \right).$$

It consists of two parts, the free vibration normally dying down after a time, and the forced vibration that takes place at the frequency of the external force. Two constants are available for the fulfilment of two boundary conditions, for instance,  $\eta = 0$  for  $\xi = a = 1$ , and  $\eta = 0$  for  $\xi = b = 1 + \lambda$ , relations holding for standing waves with an even number of loops over the length  $l$ . There follows in this case

$$\sigma c_1 D = A^+ \left( J_{\frac{1}{m+2}}(\alpha, a) J_{-\frac{1}{m+2}}(\beta, b) - J_{-\frac{1}{m+2}}(\alpha, b) J_{\frac{1}{m+2}}(\beta, a) \right) + A' \left( J_{-\frac{1}{m+2}}(\alpha, a) J_{\frac{1}{m+2}}(\beta, b) - J_{\frac{1}{m+2}}(\alpha, b) J_{-\frac{1}{m+2}}(\beta, a) \right)$$

and

$$\sigma c_2 D = A^+ \left( J_{\frac{1}{m+2}}(\alpha, b) J_{\frac{1}{m+2}}(\beta, a) - J_{\frac{1}{m+2}}(\alpha, a) J_{\frac{1}{m+2}}(\beta, b) \right) + A' \left( J_{-\frac{1}{m+2}}(\alpha, b) J_{\frac{1}{m+2}}(\beta, a) - J_{-\frac{1}{m+2}}(\alpha, a) J_{\frac{1}{m+2}}(\beta, b) \right)$$

where  $\alpha, a$ , is written for  $\alpha a^{\frac{m+2}{2}}$ , and  $\beta, b$ , for  $\beta b^{\frac{m+2}{2}}$

$$\sigma = \frac{1}{\rho_0 \pi^2 L (\nu^2 - \nu_n^2)}$$

$$D = J_{\frac{1}{m+2}}(\beta, a) J_{-\frac{1}{m+2}}(\beta, b) - J_{-\frac{1}{m+2}}(\beta, a) J_{\frac{1}{m+2}}(\beta, b).$$

As the external frequency  $\nu$  approaches  $\nu_n$ , the coefficients  $A^+$  and  $A'$ , and the expressions  $\sigma$  and  $D$ , tend toward zero, but the denominator of  $c_1$  and  $c_2$  decreases at a more rapid rate than the numerator, so that large amplitudes result even with small forces  $A^+$  and  $A'$ .

When the frequency  $\nu$  of the applied force is equal to one of the resonance frequencies  $\nu_n$  of the string, the integrals leading to the value of  $C_1(\xi)$  and  $C_2(\xi)$  appear in the indeterminate form  $0 : 0$  and must be replaced by

$$\frac{m+2}{2} \int \xi^{m+1} J_{\frac{1}{\mu}}^2(\alpha \xi^{\frac{m+2}{2}}) d\xi = \frac{\xi^{\frac{m+2}{2}}}{2} J_{\frac{1}{\mu}}^2(\alpha \xi^{\frac{m+2}{2}}) - \frac{\xi^{\frac{m+2}{2}}}{2} J_{\frac{1}{\mu}-1}(\alpha \xi^{\frac{m+2}{2}}) J_{\frac{1}{\mu}+1}(\alpha \xi^{\frac{m+2}{2}})$$

$$\frac{m+2}{2} \int \xi^{m+1} J_{\frac{1}{\mu}}(\alpha \xi^{\frac{m+2}{2}}) J_{-\frac{1}{\mu}}(\alpha \xi^{\frac{m+2}{2}}) d\xi = \frac{\xi^{\frac{m+2}{2}}}{4} (2 J_{\frac{1}{\mu}} J_{-\frac{1}{\mu}} + J_{\frac{1}{\mu}-1} J_{-\frac{1}{\mu}-1} + J_{\frac{1}{\mu}+1} J_{-\frac{1}{\mu}+1}).$$

The resulting motion is represented by

$$\frac{\eta}{\sqrt{\xi}} = c_1 J_{\frac{1}{m+2}}(\alpha \xi^{\frac{m+2}{2}}) + c_2 J_{-\frac{1}{m+2}}(\alpha \xi^{\frac{m+2}{2}}) - \frac{1}{2(m+2)L\rho_0\nu^2} \left( A^+ J_{\frac{1}{m+2}}(\alpha \xi^{\frac{m+2}{2}}) + A' J_{-\frac{1}{m+2}}(\alpha \xi^{\frac{m+2}{2}}) \right).$$

For a string of finite length both the free and the forced motion, therefore, satisfy the boundary conditions.

The shapes of the fundamental and of the first and second overtones are illustrated for  $m = 2$  (square law) and  $Q = 4$  in Fig. 1 and for  $Q = 16$  in Fig. 2. The forces necessary to maintain these standing waves are also plotted in arbitrary units. As a comparison, the shape of a sinusoidal wave, the third harmonic, is shown with the second overtone.

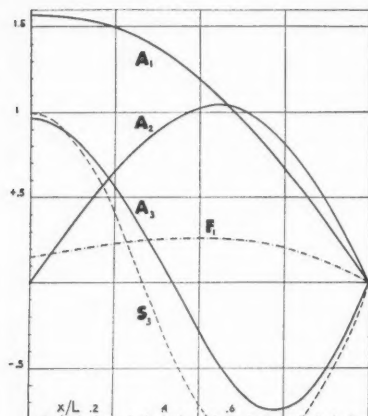


FIG. 1. Wave-shapes  $y/L$  when  $Q = 4$  for the fundamental ( $A_1$ ), the first ( $A_2$ ) and second overtone ( $A_3$ ), the sinusoidal wave ( $S_3$ ), and the force  $F_1$  required to maintain  $A_1$ .

$$A_1 = 0.807 \sqrt{\xi} J_{3/4} \left( 0.79 \times 0.75 \xi^{\frac{m+2}{2}} \right) + \sqrt{\xi} J_{-3/4} \left( 0.79 \times 0.75 \xi^{\frac{m+2}{2}} \right)$$

$$A_2 = 2 \sqrt{\xi} J_{3/4} \left( 0.79 \times 1.3 \xi^{\frac{m+2}{2}} \right) - 2.28 \sqrt{\xi} J_{-3/4} \left( 0.79 \times 1.3 \xi^{\frac{m+2}{2}} \right)$$

$$A_3 = 2 \sqrt{\xi} J_{3/4} \left( 0.79 \times 2 \xi^{\frac{m+2}{2}} \right) - 0.8 \sqrt{\xi} J_{-3/4} \left( 0.79 \times 2 \xi^{\frac{m+2}{2}} \right)$$

$$F_1 = \xi^m A_1 / 10.$$

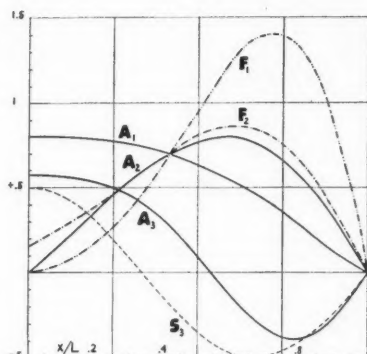


FIG. 2. Wave-shapes  $y/L$  when  $Q = 16$  for the fundamental ( $A_1$ ), the first ( $A_2$ ) and second ( $A_3$ ) overtone, the sinusoidal wave ( $S_3$ ), and the forces required to maintain  $A_1$  and  $A_2$ .

$$A_1 = 0.5 \sqrt{\xi} J_{-3/4} \left( 0.26 \times 0.5 \xi^{\frac{m+2}{2}} \right)$$

$$A_2 = \sqrt{\xi} J_{3/4} \left( 0.26 \times 0.76 \xi^{\frac{m+2}{2}} \right) - 0.43 \sqrt{\xi} J_{-3/4} \left( 0.26 \times 0.76 \xi^{\frac{m+2}{2}} \right)$$

$$A_3 = 0.24 \sqrt{\xi} J_{3/4} \left( 0.26 \times 1.3 \xi^{\frac{m+2}{2}} \right) + 0.33 \sqrt{\xi} J_{-3/4} \left( 0.26 \times 1.3 \xi^{\frac{m+2}{2}} \right)$$

$$F_1 = \xi^m A_1 / 10$$

$$F_2 = \xi^m A_2 / 5.$$

### Resonance of a Dampened String with Strengthened Ends

The response of a strengthened string subject to a dampening force during its motion can be determined with the aid of the general equations by introducing the complex pulsation  $w = 2\pi\nu + ik$ . Since however the free vibrations



die down in the course of time, the boundary equations are fulfilled only on the two conditions that the forced vibration takes place at the frequency of the external force and also in the simple shape of standing waves, whatever the frequency.

On the assumption that a solution exists in the form

$$y(x, t) = Y(x) \cos (pt - \epsilon)$$

for the equation of motion

$$\frac{\partial^2 y}{\partial t^2} = \frac{T}{\rho} \frac{\partial^2 y}{\partial x^2} + \frac{F}{\rho} \cos 2\pi \nu t - \frac{R}{\rho} \frac{\partial y}{\partial t}$$

and writing

$$F \cos pt = F \cos 2\pi \nu t = F \cos ((pt - \epsilon) + \epsilon)$$

a relation is obtained that contains  $\sin (pt + \epsilon)$  and  $\cos (pt + \epsilon)$ . Since this relation must hold for all values of  $t$ , the terms containing the factor  $\sin (pt + \epsilon)$  and the terms containing the factor  $\cos (pt + \epsilon)$  must separately add up to zero, so that

$$\frac{d^2 Y}{dx^2} + p^2 \frac{\rho}{S} Y + \frac{F(x)}{S} \cos \epsilon = 0,$$

and, regardless of any variation of the mass  $\rho$  per unit length along the string,

$$Y(x) = \frac{F(x)}{Rp} \sin \epsilon \quad (\text{providing that } \epsilon \neq 0)$$

so that

$$\tan \epsilon = \frac{RpY/\rho}{\frac{S}{\rho} \frac{d^2 Y}{dx^2} + p^2 Y}.$$

The angle by which the motion lags in phase behind the applied force is independent of the law for  $F(x)$  but varies with the relation that exists between  $Y''$  and  $Y'$ , the two variables that appear in the equation of the free motion of the string. When, in particular, the span of length  $l$  vibrates under the influence of the external force in the same manner as an undamped string, then

$$\frac{S}{\rho} \frac{d^2 Y(x)}{dx^2} = -\omega^2 Y(x) \quad \text{and} \quad Y = \rho \frac{\cos \epsilon F(x)}{\omega^2 - p^2}$$

$$\tan \epsilon = \frac{Rp/\rho}{\omega^2 - p^2}$$

$$\sin \epsilon = \frac{Rp/\rho}{\sqrt{(\omega^2 - p^2)^2 + R^2 p^2 / \rho^2}},$$

where  $\omega$  is one of the pulsations  $2\pi \nu_n$  that correspond to the resonance frequencies  $\nu_n$  of the undamped string of length  $l$ . The losses caused by friction are exactly balanced by the applied force. Though this force may

have any frequency, its strength must vary with  $x$  in proportion to the amplitudes of one of the standing waves of the freely vibrating string, because

$$Y(x) = \frac{F(x)}{R\rho \sin \epsilon} = \frac{F(x)}{\rho \sqrt{(\omega^2 - p^2)^2 + R^2 p^2 / \rho^2}}.$$

$$\text{With } F(x) = (1 + \lambda x/L)^{m+1/2} \left( A^+ J_{\frac{1}{m+2}} \left( \alpha \xi^{\frac{m+2}{2}} \right) + A' J_{-\frac{1}{m+2}} \left( \alpha \xi^{\frac{m+2}{2}} \right) \right),$$

that is, if the force varies along the string at the same rate as the product of the mass and the amplitude of the free vibrations, whatever law these vibrations may obey, and if

$$R(x) = R(1 + \lambda x/L)^m$$

at least approximately, while  $\alpha = \frac{\pi}{\lambda(m+2)} \frac{\nu}{\nu_0} = \frac{p}{2\lambda(m+2)\nu_0}$ , then

$$Y(x) = \frac{A^+ \sqrt{\xi} J_{\frac{1}{m+2}} \left( \alpha \xi^{\frac{m+2}{2}} \right) + A' \sqrt{\xi} J_{-\frac{1}{m+2}} \left( \alpha \xi^{\frac{m+2}{2}} \right)}{\rho_0 \sqrt{(\omega^2 - p^2)^2 + R^2 p^2 / \rho_0^2}}$$

so that undistorted resonance becomes possible. It will be seen that it is more difficult to fulfil the conditions for resonance in strengthened strings than in uniform strings, so that the amplitudes of vibration are reduced.

In practice, owing to the complicated changes in the amplitude that accompany higher overtones, only forces corresponding in distribution to the amplitudes of the fundamental frequency  $\nu_1$  need be considered, and, in special instances, only one of the functions  $J_{\frac{1}{(m+2)}}$  or  $J_{-\frac{1}{(m+2)}}$ .

### Special Solutions

The complete solution of the equation

$$\frac{d^2 Y}{dx^2} + \frac{4\pi^2 \nu^2 \rho_0}{S} Y = 0$$

for the shape of the vibratory string of uniform mass per unit length is

$$Y(x) = C^+ \epsilon^{\frac{2\pi i \nu}{c} x} + C' \epsilon^{-\frac{2\pi i \nu}{c} x}.$$

On the assumption that the ends of the string at  $x = a$  and at  $x = b$  are stationary, the values obtained for  $C^+/C'$  at these two points lead to the equation  $\cos 2\pi \nu(b - a)/c = 0$ , and give for the allowed frequencies the formula

$$\nu_n = \frac{n}{2l} \sqrt{\frac{S}{\rho_0}}.$$

This same result is obtained for either  $C^+$  or  $C'$  equal to zero. When similar calculations are carried out for the string with strengthened ends, the solutions secured for a vanishing  $A^+$  or  $A'$  are found to differ from the solutions that are valid when neither  $A^+$  nor  $A'$  is negligible. The assumptions that  $A'$ ,

for instance, is zero, and that the points  $x = 0$  and  $x = L$  remain at rest, give

$$J_{\frac{1}{m+2}}\left(\frac{\pi/\lambda}{m+2} \frac{\nu}{\nu_0}\right) = 0 \quad \text{at } x = 0$$

and

$$J_{\frac{1}{m+2}}\left(\frac{\pi/\lambda}{m+2} \frac{\nu}{\nu_0}(1+\lambda)^{\frac{m+2}{2}}\right) = 0 \quad \text{at } x = L,$$

whereas when the string is at rest only at  $x = L$ , but has a loop at  $x = 0$ ,

so that for  $\eta = \sqrt{\xi} J_{\frac{1}{m+2}}\left(\frac{\pi/\lambda}{m+2} \frac{\nu}{\nu_0} \xi^{\frac{m+2}{2}}\right)$

$$\frac{\partial \eta}{\partial \xi} = \frac{\nu}{2\nu_0} \frac{\pi}{\lambda} \xi^{\frac{m+1}{2}} J_{-\frac{1}{m+2}}\left(\frac{\pi/\lambda}{m+2} \frac{\nu}{\nu_0} \xi^{\frac{m+2}{2}}\right) = 0 \quad \text{at } x = 0 \text{ or } \xi = 1,$$

there follows the additional solution

$$J_{-\frac{m+1}{m+2}}\left(\frac{\pi/\lambda}{m+2} \frac{\nu}{\nu_0}\right) = 0.$$

A third series of frequencies satisfying the boundary conditions is obtained for the alternative  $A^+ = 0$  by merely changing the sign of the parameters of the three Bessel functions. With the exception of the two or three smallest solutions, the roots of the Bessel functions  $J_\mu(z)$  are given quite closely by the values following from the asymptotic expansion of  $J_\mu(z)$  and lead to the result

$$z = (2\mu + 1 \mp 2k), \text{ where } k = 1, 3, 5, \dots$$

The resonance frequencies  $\nu$  obtained from the roots of  $J_{\pm 1/(m+2)}$  and  $J_{\pm(m+1)/(m+2)}$ , or from  $J_0$  and  $J_1$  when  $m$  is very large, differ slightly from the solutions that follow from the complete equation for standing waves with an odd or an even number of loops. The complete equation contains the new solutions as a simple and evident choice that fulfils the boundary conditions when the external force lacks components of the form  $A^+J_\mu$  or  $A^-J_{-\mu}$ .



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## A STUDY OF THE DETERMINATION OF VITAMIN A BY SPECTROPHOTOMETRY AND BY PHOTOELECTRIC COLORIMETRY<sup>1</sup>

By W. D. MCFARLANE<sup>2</sup> AND A. J. SUTHERLAND<sup>3</sup>

### Abstract

A comparison has been made of the determination of vitamin A in cod-liver oils and concentrates of vitamin A by means of (a) extinction coefficient measurements at 3280 Å, and (b) photoelectric colorimetry. Both methods are shown to yield results of equal accuracy, but with cod-liver oils special precautions have to be taken in the preparation and purification of the unsaponifiable fraction. No significant difference was found between the means of the quotients, blue value/E value, for low potency cod-liver oils and those for concentrates.

The estimation of vitamin A by direct spectrophotometric measurements before and after its destruction by intense ultra-violet irradiation has been investigated. The conditions are described which permitted the complete destruction of vitamin A in a concentrate with apparently no significant effect on the other absorbing constituents of the oil except carotene. The residual absorption after irradiation amounted to about 5% of the initial absorption. With cod-liver oils the values obtained by this method are 20 to 30% lower than those obtained by absorption measurements on the unsaponifiable fraction. The results obtained with the concentrate indicate that a correction may be applied which reduces the discrepancy to about 10 to 15%.

### Part I. A Comparison of the Spectrophotometric Method and the Photoelectric Colorimetric Method of Determining Vitamin A

Two methods have been proposed as satisfactory alternatives for the biological assay of vitamin A, namely: (a) colorimetric determination—measurement of the intensity of the blue color produced when antimony trichloride dissolved in chloroform is added to a chloroform solution of the unsaponifiable portion of the oil (blue value); and (b) spectrophotometric determination—measurement of the intensity of absorption of ultra-violet radiations of wave-length 3280 Å by an alcohol or cyclohexane solution of the unsaponifiable portion of the oil (E value).

Crews and Cox (5) applied these two methods simultaneously to a series of oils and concentrates. They found that the ratio, blue value/E value, for the unsaponifiable portion of cod-liver oils is about 30, but for concentrates the value is approximately 50. Similar results have been recorded by several workers, notably Morgan *et al.* (14), who conclude that the principal sources of

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error are (a) the presence in the unsaponifiable fraction of substances other than vitamin A which absorb in the near ultra-violet or inhibit the blue color reaction, and (b) the inefficiency of the tintometer as an instrument for measuring the transient blue color. Haines and Drummond (8) analyzed halibut-liver oils by the two methods and obtained results that were in good agreement. Josephy (12) concluded that the two measurements agree with a mean error of less than 5%, and Black *et al.* (2) arrived at a similar conclusion with regard to colorimetric and vitameter measurements.

Since 1934, when the International Committee (11) approved only the ultra-violet absorption measurement as an alternate to biological assay, this method has found particular favor. The physical method was adopted in preference to the colorimetric solely because the absorption at 3280 Å could be measured with greater accuracy. Dann and Evelyn (6) recently reported that when the Evelyn photoelectric colorimeter is employed the extinction coefficient of the blue solution at 6200 Å is a linear function of the concentration of vitamin A. They clearly define the conditions that permit measurements of the blue color being made with an error of only 0.85% as compared with an acknowledged error of 10 to 15% in the Lovibond tintometer readings. It would appear therefore that the principal objection to the acceptance of the blue value as a measure of vitamin A has been removed. They have also determined the photoelectric blue value and the *E* value of 21 oils and 18 concentrates, and they find a much greater disagreement between the two values than was recorded by earlier workers. It must therefore be concluded that there may arise in either method, or in both, errors that are of much more significance than those eliminated by refinement in colorimetric technique. The method of saponification employed by Dann and Evelyn required three washings of the ether extract containing the unsaponifiable fraction with water only, whereas the British Pharmacopoeia recommends that the ether extract be washed twice with *N*/2 potassium hydroxide and three times with water. It has been our experience that the unsaponifiable fraction of some oils may be difficult to purify, hence the use of a standard saponification process for all samples may lead to errors of such magnitude that the true relation between the blue value and the *E* value will be obscured. Wilkie (16) points out that if reproducible blue values or *E* values are to be obtained the ethereal extract containing the unsaponifiable material must be washed, alternately, with dilute alkali and water until the washings fail to show any trace of precipitate when acidified with dilute hydrochloric acid.

### Experimental

In this study the photoelectric blue values and the *E* values of 16 cod-liver oils and 15 concentrates which include 6 halibut-liver oils, 4 high-potency fish oils, and one sample of vitamin distillate have been determined. In the analyses of the concentrates about 100 mg. of the oil was weighed directly into a 25 ml. volumetric flask and dissolved in a mixture of 90 parts of absolute ethyl alcohol and 10 parts of cyclohexane, and the solution was diluted to

volume with this solvent. The blue reaction was carried out according to the method of Dann and Evelyn (6), an aliquot portion of the solution (or of a more dilute solution in the same solvent) being transferred to the colorimeter tube and evaporated to dryness *in vacuo*, and the residue taken up in 1 ml. of pure anhydrous chloroform for the colorimetric determination.

The spectrographic measurements were made with a large quartz spectrograph, Littrow mounting, with 30° quartz prism and lens of 1800 mm. focal length. The dispersion was approximately 2.5 Å per mm. at  $\lambda 2500$  and 25.0 Å per mm. at  $\lambda 5500$ . The spectrograph was fitted with a Bellingham and Stanley single-disc rotating sector photometer (1936 design). Illumination was effected by a condensed spark between tungsten-steel electrodes 4 mm. apart. The spectrograms were recorded on Eastman No. 40 (8 by 10 in.) plates. The plate was examined visually with the aid of a magnifying glass, and the exposure on which the points of equal density became coincident was marked. The reading was checked by re-examining the image of the spectrogram projected on a lantern screen. It was found that no greater accuracy in reading was to be obtained by using a photoelectric densitometer. From the blue-color readings obtained with the Evelyn photoelectric colorimeter it was possible to determine the dilution of the original solution with which the matching density at 3280 Å would come on a plate covering density settings of the photometer from 0 to 0.15 by steps of 0.01. Thus the total duration of exposure of the oil to ultra-violet radiations was the same for each sample and was reduced to a minimum. The error in reading a single plate did not exceed 3%. After preparation of the solution of the oil the two estimations were carried out without delay.

The first determinations on cod-liver oil were made with a fresh sample of the "standard-of-reference oil" of the U.S. Pharmacopoeia. Saponification was carried by the procedure recommended by Wilkie (16) with the exception that petrol ether was used instead of ethyl ether. Less difficulty was experienced with the formation of emulsions when petrol ether was used to extract the unsaponifiable fraction. Occasionally a precipitate formed at the interface and prevented a complete separation of the two phases. This difficulty can be overcome by adding a few drops of 95% ethyl alcohol to the ether layer. Vaseline contains ingredients that absorb strongly at 3280 Å; consequently it should not be used to lubricate the stopcock of the separatory funnel. A paste of cane-sugar and glycerol was found to be a safe and efficient lubricant. The thoroughly washed ether extract was distilled *in vacuo* in an all-glass distilling apparatus that permitted the solvent (absolute-alcohol-cyclohexane mixture) being introduced through a side-arm before the vacuum was released. After examination of the contents of the flask in a good light to ascertain that all the residue was dissolved, the solution was transferred to a volumetric flask and made up to volume. Blue-value and *E*-value determinations were carried out in the same manner as with concentrates. The

following is a summary of the results of the determinations on the unsaponifiable fraction of the U.S.P. Reference Oil:—

I. *Blue value*

(a) Nine determinations on solutions of different concentrations of the same unsaponifiable fraction.

Range of galvanometer readings 15 to 69,  $57.4 \pm 0.48$ .

(b) Four determinations on different samples of the oil,  $55.9 \pm 0.87$ .

II. *E value* (E 1%, 1 cm., 3280 Å)

Eight determinations with different samples of the oil,  $1.36 \pm 0.0072$ .

Ratio, blue value/*E value* = 41.1.

The results of the antimony trichloride test were actually calculated as the *L* value of the oil [See Dann and Evelyn (6)] and multiplied by 20 to give the blue value. It may be concluded from these results that the determinations can be carried out on different samples of the same oil with a high degree of precision. Our *E* value for the reference oil is virtually identical with the value  $1.35 \pm 0.0053$  (10 observations) recently recorded by Barthen and Leonard (1).

Table I shows our results obtained with oils and concentrates, together with those of other workers which have been recalculated for purposes of comparison. It will be noted that our results, in contrast to the others, show no significant difference between the means of the ratios B.V./*E* for low

TABLE I  
RESULTS OF SPECTROPHOTOMETRIC AND COLORIMETRIC DETERMINATIONS OF VITAMIN A  
IN COD-LIVER OILS AND CONCENTRATES

	Nature and number of samples	Range of blue values	Ratio $\frac{\text{B.V.}}{E}$	
			Range	Mean
	<i>Cod-liver oils</i>			
Crews and Cox	10	12 - 46	19 - 30	$27.2 \pm 1.26$
Authors	16	22 - 70	34.4 - 42.3	$39.4 \pm 0.47$
	<i>Concentrates</i>			
Crews and Cox	32	530 - 80,000	39.0 - 66.7	$51.6 \pm 0.79$
Authors	15	1002 - 7,150	39.2 - 41.4	$40.5 \pm 0.12$
Haines and Drummond	5	600 - 3,440	52.0 - 55.7	$53.2 \pm 0.47$
	<i>Cod-liver oils and concentrates</i>			
Crews and Cox	42	12 - 80,000	19 - 66.7	$45.8 \pm 1.28$
Authors	31	22 - 7,150	34.4 - 42.3	$39.9 \pm 0.25$
Dann and Evelyn	39	—	—	$48.8 \pm 5.95$



potency cod-liver oils as compared to concentrates. The absolute value of the mean, but not its probable error, depends on the factor employed to convert *L* values to blue values. However the average value of approximately 40 for the ratio B.V./*E* is very close to that obtained for pure vitamin A if its blue value is taken as 80,000 (3) and its *E* value as 2100 (10). The correlation between the results of the two methods as applied to concentrates is excellent, the average error of a single determination being only about  $\pm 1\%$ . It would appear, therefore, that the same entity is being measured quantitatively in both methods. To convert their *L* values to *E* values, Dann and Evelyn recommend multiplying by  $0.41 \pm 0.05$ . The factor obtained by us was  $0.50 \pm 0.01$ .

With cod-liver oils the relation is not quite so good, the average error of a single estimation being about  $\pm 6\%$ . An error of this magnitude indicates, however, a decided improvement in technique over that available to Crews and Cox, which gave an error of  $\pm 19\%$ .

With several oils, and with two in particular, a low value for the ratio B.V./*E* was first obtained when the saponification had been carried out by the British Pharmacopoeia procedure. The determinations were repeated with more thorough washing of the unsaponifiable fraction, the result being that the *E* value was now decidedly lower, whereas the blue value was not appreciably altered. With the two most refractory oils as many as 14 alternate washings with 15 ml. portions of *N*/6 potassium hydroxide and 100 ml. portions of water were required before the ratio B.V./*E* approximated that for concentrates.

The general conclusion is that vitamin A can be determined with equal accuracy either by photoelectric colorimetry or by ultra-violet spectrophotometry, the main source of error being inherent in the saponification process.

## Part II. The Estimation of Vitamin A from Spectrophotometric Measurements before and after its Destruction by Irradiation

It is well known that a significant part of the total absorption by an oil is due to substances other than vitamin A. Even when the absorption due to unsaturated fatty acids is eliminated by employing the unsaponifiable fraction of the oil for the absorption measurement, the error due to foreign absorbents may still be considerable, particularly if the unsaponifiable fraction has not been adequately purified. The magnitude of the irrelevant absorption was pointed out by Macwalter (13) who found that approximately 40% of the absorption by a cod-liver oil was due to impurities which, unlike vitamin A, were not destroyed by oxidation for five hours at 100° C.

Obviously, quantitative estimation of vitamin A by absorption spectroscopy is possible only when the amount of the irrelevant absorption can be accurately determined. If the absorption by vitamin A could be eliminated without affecting the absorption by other substances, it would be possible to estimate the absorption due to vitamin A alone. The vitamin A content of an oil

could thus be determined directly without resort to saponification and the laborious and time-consuming purification of the unsaponifiable fraction. A simpler and more reliable measurement that would be free from the errors inherent in the saponification process would be obtained.

Several attempts have been made to make the spectrophotometric method more accurate by correcting for the irrelevant absorption. Notevarp (15) first suggested that it might be possible to destroy vitamin A quantitatively by intense irradiation of an alcoholic solution of the oil. He found oxidation and heating to be an uncertain method of removing vitamin A, and stated that when fat was present, an actual increase in absorption resulted from this treatment. In his experiments vitamin A was destroyed by irradiation with a 500 watt Orsam "Vitalux" lamp, the solution being placed about 4 cm. from the surface of the lamp for about six hours. No reference was made to the effect of this treatment on the other absorbing constituents of the oil. It was not shown that the residual absorption after irradiation was equivalent to the absorption by constituents of the oil other than vitamin A. The subject was to be treated in more detail at a later date.

More recently Chevallier (4) found that vitamin A could be accurately determined by dissolving the oil in alcohol, measuring the light absorption, irradiating with a mercury-vapor lamp fitted with a Wood's filter, again measuring the absorption, and multiplying by 3, the diminution of intensity of the absorption at 3280 Å. In support of the method it was stated that when a solution of pure vitamin A in ethyl alcohol had been subjected to intense irradiation the remaining absorption amounts to two-thirds of the initial absorption. The exact procedure used in irradiation and the details of the experiments were not given.

In our experience the destruction of vitamin A is a very slow process when alcohol is used as the solvent and when fat is present in the solution. It is well known that the vitamin is much less stable in chloroform solution (7), and for this reason alcohol or cyclohexane is now always used as the solvent for absorption measurements. It would appear therefore that the photochemical decomposition of vitamin A would be more rapid and complete if chloroform were used as the solvent.

Selective absorption of ultra-violet radiations is a characteristic property of unsaturated compounds and particularly of a molecule with a conjugated system of double bonds. Compounds of this nature that are present in liver oils are various phenanthrene derivatives, unsaturated fatty acids, carotene, and vitamin A. The unsaturated fatty acids and sterols show maximum absorption at wave-lengths less than 3000 Å; carotene, at 4500 Å. All these compounds, however, show a small end-absorption at 3280 Å. It should be possible to determine whether vitamin A alone is being oxidized, by following simultaneously the changes during irradiation in the absorption coefficient; in the blue color given by antimony trichloride; the iodine absorption value; and the carotene content of the oil. In the experiments described below, this has been done, a concentrate of the unsaponifiable material of a fish-liver

oil being used. It is shown that, under certain conditions of irradiation when a light-filter is employed that transmits ultra-violet rays of 3000 to 4000 Å only, vitamin A alone is oxidized to any significant extent, and that after the complete destruction of vitamin A the residual absorption does not exceed 10% of the original absorption. Some preliminary experiments on the destruction of vitamin A in cod-liver oils by irradiation are also discussed.

### Experimental

Irradiation was carried out with a Hanovia quartz mercury-vapor arc, which was covered by a reflector and set horizontally at a height of 10 cm. above a small cylindrical tin can (6 by 6 cm.) in which was placed a 50 ml. beaker containing the solution to be irradiated. The can was covered with a Corning red-purple-ultra No. 597 light filter (8 by 8 cm.). This filter has a light transmission of 90% at 3650 Å and 30% at 3300 Å. It is not transparent below 3000 Å or above 4000 Å but transmits again in the region of 7200 Å. It has a high thermal coefficient of expansion and is easily broken by heat. Throughout the irradiation the filter was kept cool by means of a stream of running water. Strips of adhesive tape around the filter caused the water to drain off without wetting the interior of the can.

Solutions of vitamin A were prepared by weighing about 30 mg. of the concentrate into the beaker and dissolving in 5 ml. of anhydrous chloroform. The solutions were irradiated for varying lengths of time, the lamp current being maintained at 3.5 amp., 220 d.c. Each solution was finally transferred to a 25 ml. volumetric flask and made up to volume with chloroform. The following determinations were carried out, without delay, on aliquots of each solution.

1. *Extinction Coefficient.* A 5 ml. aliquot of the solution was evaporated *in vacuo* to dryness. The residue was taken up in absolute-ethyl-alcohol-cyclohexane mixture (90 : 10) and diluted to the required volume with this solvent. The value  $E_{1\text{ cm.}}^{1\%}$  at 3280 Å was determined by the procedure already described in Part I. The residue from 5 ml. of chloroform alone showed a small absorption at 3280 Å for which a correction was made.

2. *Antimony Trichloride Reaction.* The blue reaction and the colorimetric determination of the intensity of the blue color were carried out by the procedure of Dann and Evelyn (6). A 2 ml. aliquot of the solution was diluted to 10 ml. with chloroform, and 1 ml. of this solution was taken for the determination.

3. *Iodine Absorption.* The determination was made by the Hanus method, a 5 ml. aliquot of the solution, a 30 min. absorption period, and *N*/50 iodine and sodium thiosulphate solutions, being used.

4. *Carotene Content.* The yellow color of the solutions was assumed to be due entirely to carotene. Readings of the intensity of the yellow color were made with an Evelyn photoelectric colorimeter, and the carotene equivalent was obtained by reference to a calibration curve that had been previously prepared by use of standard solutions of  $\beta$  carotene.

Following the investigation of the effect of irradiating solutions of the concentrate, the procedure was applied to four cod-liver oils. In each determination 0.1 gm. of the oil was dissolved in 5 ml. of anhydrous chloroform and the solution irradiated for one hour in the manner described above. Determinations were made of the extinction coefficient of the oil at 3280 Å before and after irradiation and also on the non-saponifiable fraction of the oil. Measurements of blue-color reactions and iodine absorption were also made at varying intervals during the irradiation of one oil.

In Fig. 1 are plotted the absorption curves obtained before and after irradiation of the concentrate. The results of irradiation for two hours were virtually identical with those of 1½ hours' irradiation. It may be concluded,

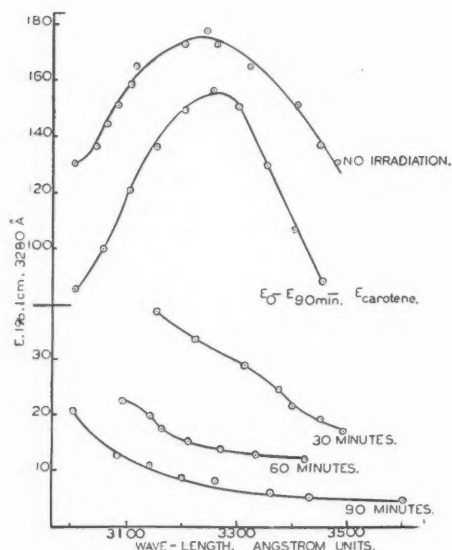


FIG. 1. Effect of irradiation on the ultra-violet absorption of a concentrate of vitamin A.

curve of carotene as given by Heierle (9). Prior to irradiation the carotene content of the solution was 0.76 mg., and after one hour irradiation it was reduced to 0.30 mg. per gm. of concentrate.

The results indicate that irradiating for one hour results in a complete destruction of vitamin A without affecting to any significant extent the other absorbing constituents with the exception of carotene. This is further substantiated by the results presented in Fig. 2 which show that the blue-color reaction of the concentrate is destroyed by irradiation for one hour and that, in general, during irradiation the changes in the blue value and absorption value parallel each other. A slight lag in the destruction of vitamin A during

therefore, that after irradiation for one hour the absorption at 3280 Å had virtually reached a minimum value and underwent a further reduction of only about 3% after irradiation for an additional hour. Also shown in Fig. 1 is the curve obtained after subtraction from the value for the initial absorption the absorption due to carotene plus the residual absorption after 90 min. irradiation. This curve fits, extremely well, the curve obtained when the absorption curve of pure vitamin A, as given by Holmes and Corbet (10), is reduced to the same absorption maximum. The values for the absorption of carotene between 3000 and 4000 Å were calculated from the ultra-violet absorption

the initial period of irradiation is observed. It will be noted further that, although the results given in Figs. 1 and 2 were obtained with the same concentrate, the absorption by the two solutions before irradiation is not the same. A period of several months intervened between the two experiments, and during this time the small amount of concentrate underwent considerable oxidation.

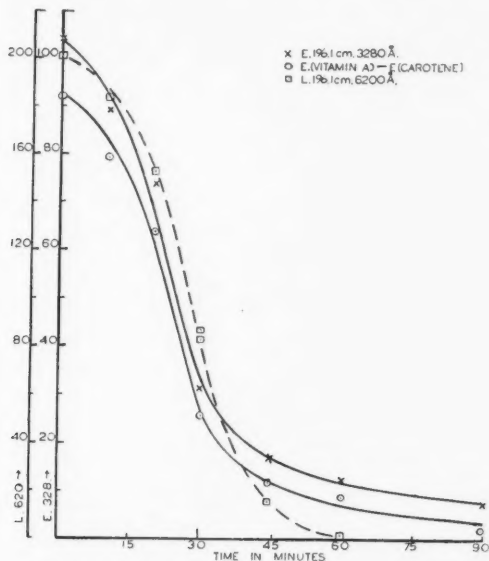


FIG. 2. Effect of irradiation on the blue-color reaction (*L* value) and ultra-violet absorption (*E* value) of a concentrate of vitamin A.

Though the iodine absorption value of the concentrate (Fig. 3) undoubtedly diminished most rapidly during the first hour of irradiation, when vitamin A was undergoing rapid photo-chemical oxidation, it still continued to decrease after a negative blue-color reaction was obtained. The decrease in iodine absorption due to the oxidation of carotene is not known, but it is believed to be negligible.

In Table II are summarized the results of the absorption measurements carried out with cod-liver oils before and after their irradiation. Those referred to as being obtained by a "modified photometry" were made with the irradiated solution in the tube on the variable-aperture side of the sector photometer (which ordinarily contains the solvent only) and a solution of the untreated oil in the tube on the fixed-aperture side of the photometer. This procedure was first introduced by De (7). The results obtained by this method, as is to be expected on theoretical grounds, are in good agreement with those obtained by taking the difference between two separate absorption

TABLE II  
RESULTS OF EXTINCTION COEFFICIENT MEASUREMENTS ON COD-LIVER OILS BEFORE AND AFTER ULTRA-VIOLET IRRADIATION

Sample No.	$E_{1\text{ cm.}}^{1\%}, 3280 \text{ \AA}$				
	Before irradiation	After irradiation	By difference	By modified photometry	Unsaponifiable fraction
38-279	1.39	0.54	0.85	0.85	1.24
38-280	1.41	0.46	0.95	0.91	1.26
37-556	1.42	0.40	1.02	1.06	1.30
38-305	3280	1.50	1.05	1.02	1.34
	3198	1.59	1.14	—	—

measurements before and after irradiation. It will be noted further that these values are about 20 to 30% lower than those obtained by direct measurement on the unsaponifiable fraction. Sample No. 38/305 is the U.S.P. reference oil, which officially contains 3000 International Units of vitamin A.

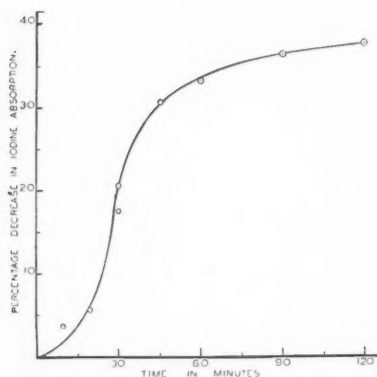


FIG. 3. Effect of irradiation on the iodine absorption by a concentrate of vitamin A.

its  $E$  value (by difference) would now become 1.18, which is still 12% less than the value for the unsaponifiable fraction. From the results obtained with the concentrate it was expected that the  $E$  value (by difference) would have tended to be higher than that of the unsaponifiable fraction; no explanation is forthcoming for the fact that it is lower.

When absorption measurements are made directly with oils the head of the absorption band is usually displaced towards the shorter wave-lengths. This was found to be the case with all these oils; the reference oil, for example, showed maximum absorption at 3198 Å. Two values are recorded in Table II for the direct  $E$  value of the reference oil. It will be seen that

An  $E$  value of 1.02 would give a conversion factor of 2900 which, judged by present standards, would appear to be too high. During the one-hour irradiation no change in the iodine absorption number of the oil could be detected, the blue-color reaction was negative after 30 min. irradiation, and the extinction coefficient at 3280 Å had reached a minimum value after irradiation for one hour. If it is assumed that photochemical decomposition products of vitamin A are responsible for the residual absorption after irradiation of the concentrate for one hour (see Fig. 1), and if this correction of 8.5% is applied to the measurement with the reference oil,

reading the plate at 3280 Å and not at the head of the absorption band gives a corrected  $E$  value of 1.05, which is in better agreement with the  $E$  value obtained by modified photometry. The plates obtained by modified photometry always showed the maximum absorption to be very close to 3280 Å.

### Acknowledgments

The authors are indebted to Dr. A. S. Cook of the Ayerst, McKenna and Harrison Company, Montreal, for supplying the samples and for carrying out some of the blue-value determinations, and to Dr. D. K. Froman of the Department of Physics, Macdonald College, for many helpful suggestions.

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## CALYCANTHINE

III. SOME DEGRADATION EXPERIMENTS<sup>1</sup>BY LÉO MARION<sup>2</sup> AND RICHARD H. F. MANSKE<sup>2</sup>

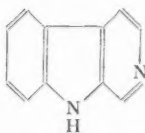
## Abstract

The identification of 4-carboline amongst the degradation products obtained by the action of selenium on calycanthine makes it possible to account for 12 of the 22 carbon atoms of calycanthine. The fusion of calycanthine with phthalic anhydride yielded 12:13-benzcanthin-11-one, which was also obtained from tryptamine and phthalic anhydride. On the basis of these observations a partial formula for calycanthine is suggested. The oxidation of calycanthine with mercuric acetate eliminated two hydrogen atoms, giving rise to a base which can be reduced again to calycanthine. Reduction of calycanthine with hydriodic acid and red phosphorus yielded quinoline, and methylation in the presence of air gave rise to oxygenated products containing three nitrogen atoms, and to methylamine. The phenylcarbamyl derivative of calycanthine has the same ultimate composition as, but differs from, that of N-methyltryptamine.

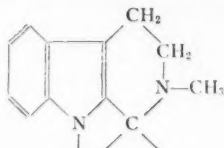
Calycanthine ( $C_{22}H_{28}N_4$ ) is the main alkaloid present in the seeds of *Calycanthus floridus* L. The formation of benzoyl-N-methyltryptamine in the oxidative degradation of calycanthine (4) accounts for one-half of the molecule only. The authors have made numerous attempts to elucidate the molecule further, and some of these are now placed on record.

Dehydrogenation with selenium yielded two basic fragments. One of these, melting at  $307^\circ C.$ ,\* is also a product of the distillation of calycanthine with zinc dust. The analytical figures indicate the formula  $C_{16}H_{10}N_2$  which probably includes the tryptamine portion of the calycanthine molecule plus six carbon atoms belonging to the remaining fragment. It gives a negative test with Ehrlich's reagent indicating that the  $\alpha$ - and  $\beta$ -positions of the indole nucleus are substituted. Its further investigation has been left in abeyance pending the accumulation of a larger supply.

The second basic fragment obtained in the dehydrogenation, first isolated as the picrate,  $C_{17}H_{11}O_7N_5$ , m.p.  $263^\circ C.$ , was eventually obtained as a well crystallized base, m.p.  $186^\circ C.$  Its solutions were fluorescent, and the analyses of both the base and its picrate indicated the formula  $C_{11}H_8N_2$ , which is that of a carboline. It has been identified as 4-carboline (I), and admixture of the picrate with that of synthetic 4-carboline failed to depress the melting point. If taken in conjunction with the production of benzoyl-N-methyltryptamine,



I.



II.

<sup>1</sup> Manuscript received November 10, 1938.

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada.

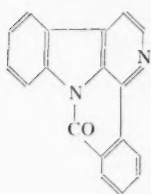
<sup>2</sup> Chemist, National Research Laboratories, Ottawa.

\* All melting points are corrected.

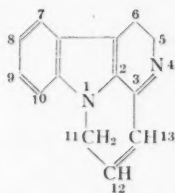


the isolation of 4-carboline as a dehydrogenation product supports the partial structure II, previously suggested by one of us (4), which accounts for 12 of the 22 carbon atoms of calycanthine.

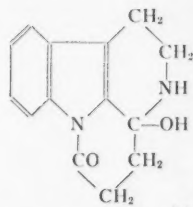
The elimination of the N-methyl of the methylcarboline portion of the molecule, in reactions involving the dehydrogenation of the tetrahydropyridine ring, illustrated by the production of 4-carboline, also occurs in the fusion of calycanthine with phthalic anhydride which yielded a basic substance,  $C_{18}H_{10}ON_2$ , m.p.  $227^\circ C$ . (The action of organic acids in eliminating an N-methyl from a base is a reaction discovered by von Braun and Weissbach (1), who obtained impure and partly racemised *l*-nornicotine on heating *l*-nicotine with hydrocinnamic acid.) This substance ( $C_{18}H_{10}ON_2$ ) gives a negative test with Ehrlich's reagent. From its ultimate composition and its mode of formation, the most probable structure seemed to be that of 12 : 13-benzcanthin-11-one (III), in which one mole of phthalic anhydride is involved. This compound (III) is named as a derivative of the hypothetical substance IV for which the generic name *canthine* is now proposed.



III.



IV.



V.

A substance probably having formula (III) has been synthesized from tryptamine and phthalic anhydride, and the synthetic product, m.p.  $227^\circ C$ , did not depress the melting point of the base obtained from calycanthine when mixed with it.

In the hope of preparing a base similar to (III), but without the benzene ring which base (III) owed to phthalic anhydride, tryptamine was fused with succinic anhydride. The product,  $C_{14}H_{14}O_2N_2$ , m.p.  $172^\circ C$ , however, contained two atoms of oxygen and reacted positively with Ehrlich's reagent, so that the  $\alpha$ - or  $\beta$ -position of the pyrrole nucleus in the product must be free or potentially so. Furthermore, the product behaved as a phenolic base and the two methylene groups originally attached to the indole nucleus in tryptamine have not been dehydrogenated. It is, possibly, 3,4,5,6,12,13-hexahydro-3-hydroxycanthin-11-one (V).

The reduction of calycanthine with hydriodic acid and red phosphorus yields quinoline. It is doubtful, however, whether this grouping exists as such in calycanthine, and its formation is possibly due to a rearrangement.

When calycanthine is oxidized with mercuric acetate according to the method of Gadamer (2), two hydrogen atoms are eliminated. This gives rise to a new base which forms an amorphous picrate. The base is easily converted back to calycanthine by reduction. The readiness with which

calycanthine is oxidized may explain the formation, on methylation, of products containing oxygen. Späth and Stroh (7) have methylated calycanthine in an evacuated tube and obtained a methiodide,  $C_{22}H_{26}N_4(CH_3)_2 \cdot 2CH_3I$ . Gordin (3), however, had found that if the methylation was conducted in the presence of air, one nitrogen atom was lost, and the product contained oxygen. It is not considered proved that the entry of oxygen into the molecule is due to the oxidation of calycanthine or of a derivative by atmospheric oxygen. The results obtained by the authors confirm those of Gordin, and the methylation of calycanthine gave rise to oxygenated derivatives containing three atoms of nitrogen only. With methyl iodide as methylating agent, products were obtained containing one, two, and three atoms of oxygen. The nitrogen atom which is lost during methylation is eliminated in the form of methylamine, which has been isolated from the mother liquors as the chloroplatinate.

Calycanthine forms a phenylcarbamyl derivative,  $C_{36}H_{35}O_2N_6$ , m.p.  $252^\circ C$ ., which corresponds to one mole of calycanthine and two moles of phenylisocyanate. The phenylcarbamyl derivative of N-methyltryptamine,  $C_{18}H_{19}ON_3$ , which has the same ultimate composition as, but is not identical with, the calycanthine derivative, melts at  $153^\circ C$ . (5). Both derivatives, however, yield an orange color in Ehrlich's test.

### Experimental

#### *Dehydrogenation with Selenium*

Anhydrous calycanthine (5.7 gm.) was heated in a metal bath with 5.7 gm. of selenium, in a stream of nitrogen. The temperature was gradually brought up to  $300^\circ C$ ., where it was kept for one-half hour. The flask and the melt, which had set to a hard resin, were crushed together in a mortar and extracted in a Soxhlet with petroleum ether and with ether. Both extracts yielded a base which, after recrystallization from methanol, melted at  $306$  to  $307^\circ C$ . This base, owing to the small quantity obtained, may be still slightly impure. Calcd. for  $C_{16}H_{10}N_2$ : C, 83.3; H, 4.34; N, 12.16%. Found: C, 82.52, 82.55; H, 4.62, 4.45; N, 12.20, 12.07%. The combined mother liquors from the crystallization of the latter base were treated with picric acid. From the mixed product, fractional crystallization yielded a picrate, m.p.  $263^\circ C$ ., as fine yellow needles. Calcd. for  $C_{17}H_{11}O_7N_5$ : C, 51.4; H, 2.77; N, 17.65%. Found: C, 51.50, 51.46; H, 3.02, 2.99; N, 16.22, 16.26%. When this substance was mixed with the picrate of 4-carboline (m.p.  $264^\circ C$ .) the melting point was not depressed. The base liberated from the picrate was crystallized from absolute ether, from which it separated as short, colorless needles, m.p.  $186^\circ C$ . Calcd. for  $C_{11}H_8N_2$ : C, 78.57; H, 4.76; N, 16.66%. Found: C, 78.66; H, 5.11; N, 16.53%.

#### *Zinc Dust Distillation*

A mixture of calycanthine and zinc dust was heated, ultimately to dull redness in a tube through which a stream of hydrogen was being passed. The distillate contained indoles in abundance together with a small amount of

crystalline material. The latter was washed with cold ethanol and recrystallized once from a large volume of the same solvent. It then consisted of fine almost colorless needles which melt at 305 to 306° C. In admixture with the substance prepared by the selenium dehydrogenation there was no depression in melting point.

#### *Synthesis of 4-Carboline*

3,4,5,6-Tetrahydro-4-carboline was prepared from tryptamine as described by Späth and Lederer (6) and dehydrogenated by heating with selenium at 300° C. for one-half hour in a stream of nitrogen. The base was extracted with ether and crystallized from the same solvent. It was then sublimed at 200° (2 mm.), and converted to the picrate which was recrystallized from methanol, m.p. 264° C.

#### *Reduction of Calycanthine*

A mixture of calycanthine (6 gm.), red phosphorus (6 gm.), and 50% hydriodic acid (45 cc.) was refluxed gently for 90 hr. and evaporated to about one-third of its volume. This was filtered, the filtrate basified, and the precipitated base collected on a filter, and dried. Distillation of this base at 200 to 260° C. (1 mm.), yielded an oil which appeared to be a mixture. It was distilled in steam and the distillate, on treatment with picric acid, yielded a picrate melting at 202 to 203° C. before and after admixture with an authentic specimen of quinoline picrate.

#### *Oxidation of Calycanthine*

To a solution of 0.3192 gm. of calycanthine in 1.5 cc. of glacial acetic acid was added 2 gm. of mercuric acetate dissolved in 15 cc. of water containing a few drops of acetic acid, according to the method of Gadamer (2). The solution was allowed to stand at room temperature for 40 hr. during which a precipitate of short needles separated. Water was added, and the mixture warmed on the steam-bath for 20 min. and allowed to stand at room temperature a further 22 hr. The precipitated mercurous acetate was filtered on a tared alundum crucible, washed with a little water, dried at 105° C., and weighed: 0.4545 gm. The elimination of two hydrogen atoms corresponds to 0.4761 gm. of mercurous acetate. Yield, 95.4%. The filtrate was acidified with hydrochloric acid and the mercury removed with hydrogen sulphide. The base recovered was oily and could not be crystallized. It yielded an amorphous picrate melting indefinitely between 105° and 135° C. All attempts to crystallize this picrate have been unsuccessful. Calycanthine picrate crystallizes from methanol in fine, silky needles, m.p. 186 to 187° C. The oxidized base is readily converted back to calycanthine by reduction with zinc and acetic acid.

#### *Treatment of Calycanthine with Phthalic Anhydride*

A mixture of calycanthine (1 gm.) and phthalic anhydride (10 gm.) was heated in an oil bath for four hours at 200° C. and five hours at 225 to 230°. After cooling, the melt was repeatedly digested with boiling water containing some hydrochloric acid. From the combined and filtered acid extracts a

base was isolated which, after several recrystallizations from acetone-methanol, was obtained as slender colorless needles, m.p. 227° C. Wt. 0.043 gm. Calcd. for  $C_{18}H_{10}ON_2$ : C, 80.0; H, 3.74; N, 10.37%. Found: C, 79.56, 79.41; H, 3.69, 3.79; N, 10.67, 10.60%.

#### *Synthesis of 12 : 13-benzcanthin-11-one*

A mixture of tryptamine (4 gm.) and phthalic anhydride (11 gm.) was heated in an oil bath, four hours at 200° C. and five hours at 230° C. The product was worked up as in the above case. It yielded a relatively large quantity of a neutral product, m.p. 165° C., identified by melting point and mixed melting point as 3-( $\beta$ -phthalimido-ethyl)-indole, and 0.029 gm. of a base which separated from acetone-methanol as fine, soft needles, m.p. 227 to 228°. Calcd. for  $C_{18}H_{10}ON_2$ : N, 10.37%; found: N, 10.51%. A mixture of this substance with the base obtained from calycanthine and phthalic anhydride melted at 227 to 228° C.

#### *Treatment of Tryptamine with Succinic Anhydride*

Tryptamine (4 gm.) and succinic anhydride (10 gm.) were heated together in an oil bath for four hours at 200° C. and five hours at 225 to 230°. The cooled melt was digested with cold dilute hydrochloric acid and the acid extract basified with ammonia. When potassium hydroxide is used instead of ammonia, the precipitated base redissolves in the basic solution. The basic product (0.142 gm.), crystallized several times from acetone-methanol, was obtained as fine, colorless needles, m.p. 172° C. Calcd. for  $C_{14}H_{14}O_2N_2$ : C, 69.42; H, 5.78; N, 11.57%. Found: C, 69.39; 69.32; H, 5.99, 5.98; N, 11.46, 11.34%.

#### *Reaction of Calycanthine with Phenylisocyanate*

The phenylcarbamyl derivative of calycanthine was obtained by heating the base in chloroform with phenylisocyanate and evaporating to dryness. The residue was digested repeatedly with cold dilute hydrochloric acid and the combined acid extracts were basified. The filtered and dried basic product separated from chloroform-methanol as colorless prisms, m.p. 252° C. Calcd. for  $C_{36}H_{38}O_2N_6$ : C, 73.72; H, 6.49; N, 14.34%. Found: C, 73.65, 73.67; H, 6.46, 6.27; N, 14.30, 14.25%.

#### *Methylation of Calycanthine*

The products obtained in the methylation of calycanthine were difficult to isolate and purify. Although the samples analyzed have been purified as carefully as possible it is not certain that they were entirely homogeneous. The analyses are reported below simply to show the constancy of the presence of oxygen and the loss of one nitrogen atom in all the methylated products. A solution of anhydrous calycanthine in chloroform when treated with methyl iodide gradually deposits a crystalline product which can be separated by difference in solubility in methanol into a methiodide, m.p. 249° C., and a second product, m.p. 235 to 237° C., also containing iodine. The latter gave the following analytical figures. Calcd. for  $C_{26}H_{32}ON_3I$ : C, 58.95; H, 6.02;

N, 7.94; I, 24.00%. Found: C, 55.47, 55.57; H, 6.01, 6.11; N, 7.97, 7.84; I, 22.77%. When hydrolyzed with aqueous-methanolic potassium hydroxide it gave rise to a compound soluble in chloroform and crystallizable from chloroform-methanol as small, white, lustrous plates, m.p. 216 to 218° C. (calcd. for  $C_{26}H_{34}O_3N_3I$ : C, 55.2; H, 6.02; N, 7.44; I, 22.5%—found: C, 55.47, 55.57; H, 6.01, 6.11; N, 7.97, 7.84; I, 22.77%), and a second compound, m.p. 243° C., insoluble in chloroform. This was crystallized from methanol. Calcd. for  $C_{26}H_{34}O_3N_3I$ : C, 57.05; H, 6.22; N, 7.68; I, 23.20%. Found: C, 55.20, 55.34; H, 6.26, 6.15; N, 7.44, 7.43; I, 24.46%.

The collected mother liquors from the methylated calycanthine were mixed with methanolic potassium hydroxide and distilled. The distillate was collected in dilute hydrochloric acid, and evaporated on the steam bath in a stream of air. It left a crystalline residue which was recrystallized from methanol-acetone and then converted into a chloroplatinate, m.p. 223 to 225° C. A mixture of this substance with methylamine chloroplatinate (m.p. 225 to 227° C.) melted at 227° C. Calcd. for  $CH_3 \cdot NH_2 \cdot H_2PtCl_6$ : Pt, 41.3%. Found: Pt, 40.4%.

When calycanthine is methylated with dimethyl sulphate in the presence of potassium carbonate, a methylated base is obtained which melts at 219° C. Calcd. for  $C_{25}H_{35}O_5N_3S$ : C, 61.33; H, 7.16; N, 8.58; S, 6.54%. Found: C, 60.72, 61.00; H, 6.88, 6.75; N, 8.54, 8.34; S, 6.52%. This base is not precipitated by potassium hydroxide from its solution in dilute acid. If, however, this solution is heated with ammonium chloride a base containing no sulphur is precipitated. Crystallized from absolute alcohol and from acetone-ether, as clusters of prismatic needles, it melted at 214 to 216° C., after sintering somewhat at 205° C. Calcd. for  $C_{24}H_{33}O_5N_3$ : C, 64.9; H, 7.44; N, 9.47%. Found: C, 63.94, 63.85; H, 7.09, 7.02; N, 9.42, 9.65%.

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## THE ALKALOIDS OF FUMARIACEOUS PLANTS

XVIII. *FUMARIA OFFICINALIS* L.<sup>1</sup>BY RICHARD H. F. MANSKE<sup>2</sup>

## Abstract

An examination of *Fumaria officinalis* has disclosed the presence of seven alkaloids. Of these, only protopine (0.05%) had been previously reported. In this plant other known alkaloids are *dl*-tetrahydro-coptisine (2.5 p.p.m.), cryptocavine (20 p.p.m.), aurotensine (0.4 p.p.m.), and possibly sinactine (22 p.p.m.) which, however, was not conclusively identified and is referred to as alkaloid F36. The remaining two alkaloids are apparently new; F37 (26 p.p.m.),  $C_{21}H_{23}O_5N$ , is non-phenolic and contains two methoxyl groups; F38 (3 p.p.m.)  $C_{20}H_{19}O_6N$ , is phenolic and is probably a phthalide isoquinoline alkaloid. A neutral substance,  $C_{17}H_{15}O_3$ , was also isolated.

Attention is directed to the significance of alkaloid structure in an evolutionary series of plants, and some preliminary generalizations are adumbrated.

If the nature of the chemical constituents of plants, and here reference is restricted to alkaloids, is a criterion of relationship, the inclusion of Fumariaceae as a sub-family in Papaveraceae is amply justified. Protopine has been isolated from no fewer than 35 species inclusive of 14 genera, but only from plants in the Papaveraceae family (11). No other alkaloid is known to have such a wide distribution, and there is ample ground for the belief that it will be found in most of the genera in this family. In fact, its complete absence in a particular species would call for more than passing comment. Other alkaloids, but noticeably cryptopine, allocryptopine, glaucine, and the protoberberine bases, are known to occur in several genera, and even in related families. Furthermore, virtually all the Papaveraceae alkaloids can be regarded as derivatives of benzyl-isoquinoline. Such a relation cannot be regarded as fortuitous and definitely suggests a common origin for all members of the Family.

On the basis of the morphology and anatomy of the vegetative organs, Leger (3) concluded that the genus *Fumaria* is phylogenetically the oldest and *Papaver* the most recent. His classification is shown schematically on the following page.

On the other hand, Fedde (1) regards the sub-family Fumarioideae as the most recent. Although the order suggested by Leger is retained, the temporal sequence is reversed. On this basis the genus *Fumaria* is to be regarded as the most recent. Such a hypothesis is consistent with the fact that no species of *Fumaria* is native to America. On this continent the endemic genus *Adlumia* was presumably evolved from *Dicentra* or a common ancestor. In Asia the corresponding scandent genus is *Dactylicapnos*.

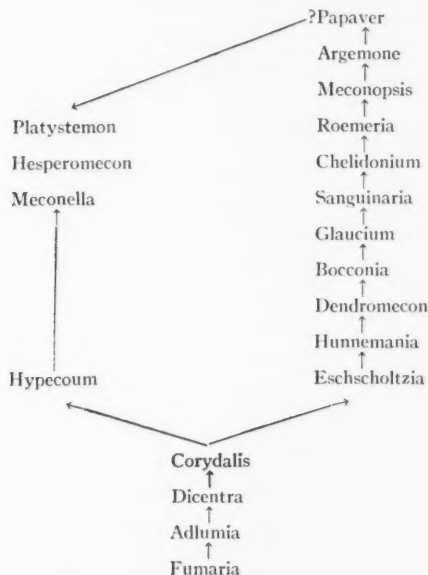
The hypothesis that progress in evolution is accompanied by an increased complexity of chemical constituents has been suggested at various times, and McNair (10) has applied such a criterion in an attempt to place the

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Angiosperms in an evolutionary sequence with reference to alkaloids. In the author's opinion it is questionable whether an acceptable criterion of complexity can be formulated. McNair suggested the average molecular weight as such a criterion, although obvious disadvantages are at once apparent. It seems more probable that taxonomic similarities and differences will be reflected in the chemical constitution of the contained alkaloids. The possibilities of testing this hypothesis by means of data accumulated in studies of the alkaloids of Fumariaceae plants, reported in this series of papers, have been kept in mind, and it now seems advisable to mention some of the conclusions which may be drawn. Dicentrine, glaucine, and glaucentrine are found together only in the Eucapnos section of *Dicentra*, namely in *D. eximia*, *D. formosa*, and *D. oregana* (5, 9). In *Corydalis* the protoberberine alkaloids are widely distributed. They are rarer in *Dicentra* and virtually absent in *Papaver*. Bicuculline and corlumine appear to be more specific and their limited occurrence may well form the basis for a reclassification. Nevertheless no satisfactory chemical criteria are available as yet which would serve to indicate the progress of evolution in Papaveraceae. Many more data are necessary and the examination of some species of *Fumaria* was deemed essential.



*Fumaria officinalis* L., with which the present paper deals, is the common fumitory of European origin, although it is now widely distributed in temperate regions. It is the type species of a genus which includes some fifty species and numerous varieties. They are native to northwestern and Central



Europe, to the region from the Mediterranean to the extra-tropical Himalaya, and to Western and Central Asia.

The plant was examined chemically shortly after the recognition of organic bases as a class of natural compounds. A number of authors have isolated an alkaloid (fumarine) which Schmidt (11) proved to be identical with protopine, although it is now doubtful whether this alkaloid was obtained in a state of purity from the plant in question.

The present investigation has disclosed that protopine, while definitely present, constitutes only a portion of the total alkaloid content, which in any case is less than 0.2%. No fewer than six other alkaloids have been isolated, and, of these, three may be new. Cryptocavine (9) and aurotensine (9) were obtained in small amounts and compared with authentic specimens from previous sources. A third alkaloid almost certainly is *dl*-tetrahydro-coptisine. Analytical data, color reactions, and the lack of optical activity are in agreement with this supposition, although direct comparison with an authentic specimen has not been made. The same alkaloid has also been isolated from *Corydalis cheilanthifolia*.

Closely associated with the *dl*-tetrahydro-coptisine is an alkaloid which resembles sinactine. Analytical data are in fair agreement with the formula  $C_{20}H_{21}O_4N$  and two methoxyl groups are indicated. It melts at  $177^\circ C.$ \* as does sinactine, but the optical rotation of  $-78.9^\circ$  is not comparable to a value of about  $300^\circ$  for the latter. In view of the frequent occurrence of racemic alkaloids in the tetrahydro-protoberberine group the alkaloid in question may represent a largely racemized specimen of sinactine. Nevertheless, reduction of the quaternary iodide, formed by oxidation with iodine in ethanol, yielded a base that melted at  $163^\circ C.$ , and repeated recrystallization did not alter this value. Späth and Mosettig (12) state that *dl*-sinactine melts at  $171^\circ C.$ , presumably uncorrected. An observation that is relevant here, and which may ultimately have more significance, is that the phenolic alkaloid F13 (9) first isolated from *Corydalis scouleri* (6) and later from *C. sibirica* (7) on methylation with diazomethane yields a base identical with this alkaloid. In fact the necessary formula,  $C_{19}H_{19}O_4N$ , is in better agreement with the analytical figures than the formulae  $(C_{16}H_{17}O_3N$  and  $C_{17(18)}H_{19}O_4N)$  previously considered. Since, therefore, the base has not been definitely identified, it will be provisionally referred to as alkaloid F36.

The remaining two alkaloids appear to be new. F37, melting at  $177^\circ C.$ , yields analytical figures in fair agreement with  $C_{21}H_{23}O_5N$  containing two methoxyl groups. This formula is homologous with that for cryptocavine. The latter is optically inactive and the remote possibility that it is the racemic form of F37 has been considered, although the color reactions are not identical. Cryptocavine is undoubtedly of the protopine type. In the case of corycavamine racemization is effected by heating with acetic anhydride. Alkaloid F37, however, did not yield cryptocavine under these conditions.

\* All melting points are corrected.



Alkaloid F38, melting at 255° C., is phenolic, contains one methoxyl group, and is best represented by  $C_{20}H_{19}O_6N$ . This formula is isomeric with that of corluminine (6). On methylation it may be expected to yield either corlumine or adlumine, but owing to the small amount available this possibility has not been tested experimentally.

### Experimental

A preliminary investigation of *F. officinalis* was carried out with 2.4 kg. of material collected in Switzerland. This was made available to the author by Dr. Richard Ruedy of these laboratories, to whom thanks are due. The main lot of material was obtained from the New York Chemical Corporation, New York. It weighed 49 kg. Cryptocavine, aurotensine, and alkaloid F38 were not isolated from the smaller lot, although there is no reason to assume that they were absent. In any case they were found only in traces in the main lot and their isolation in a pure form is tedious. The following account refers only to the 49 kg. of material. The procedure detailed in an earlier communication (4) has been followed and the same designations of the various fractions are employed. The results are summarized in the following outline:

Base hydrochlorides extracted from aqueous solution by means of chloroform—

BC —Non-phenolic bases,—*dl*-tetrahydro-coptisine, F36, F37.

EC —Phenolic bases extracted from alkaline solution by means of ether,—F37 (in part).

BCE—Phenolic bases precipitated by carbon dioxide,—uncrystallized.

Base hydrochlorides not extracted from aqueous solution by means of chloroform—

BS —Non-phenolic bases,—protopine, cryptocavine.

BSE—Phenolic bases precipitated by carbon dioxide,—aurotensine, F38.

EES—Phenolic bases extracted from the bicarbonate solution by means of ether,—aurotensine, F38.

#### *dl*-Tetrahydro-coptisine and Alkaloid F36

The non-phenolic fraction (BC) was dissolved in hot dilute hydrochloric acid and filtered. On cooling, a crop of pale yellow, fine needles separated. This, on recrystallization from much hot water was almost colorless and after drying melted at 252 to 253° C., with only slight previous sintering or darkening. Goto and Kitasato (2) record the melting point of sinactine hydrochloride as 272° C. In this property, therefore, the differences are also appreciable. The free base was regenerated by shaking an aqueous suspension of the hydrochloride with ammonia and ether, and washing the resultant ether extract. Removal of the solvent from the latter yielded a crystalline residue which was washed with cold methanol and then recrystallized from chloroform-methanol. As thus obtained *alkaloid F36* consists of well developed, stout, colorless prisms and melts sharply at 177° C. The yield was about 1.1 gm. (22 p.p.m.). Further recrystallization did not raise the melting point. With Gaebel's reagent it gives a positive test for the methylenedioxy group.  $[\alpha]_D^{23} = -78.9^\circ$  ( $c = 0.4$  in chloroform). Found: C, 70.25, 70.40; H,

6.21, 6.44; N, 4.87; 4.99; OMe, 18.86, 18.54%. Calcd. for  $C_{20}H_{21}O_4N$ ; C, 70.80; H, 6.20; N, 4.38; OMe, 18.20%.

A small portion of the alkaloid, dissolved in boiling ethanol containing some potassium acetate, was treated with iodine until the color due to the latter was permanent. Some water was added and the ethanol boiled off. The dark brown iodide as thus obtained was washed with cold water and its brown solution in hot glacial acetic acid was treated with zinc dust until it was colorless. The base was regenerated from the filtered solution by means of ammonia and extracted with ether. Evaporation of the extract yielded an almost colorless resin which readily crystallized in contact with methanol. It melted at  $163^{\circ}\text{C}$ . and this value was not changed after three further recrystallizations from methanol. Determination of the melting point in an evacuated tube gave the same value.

The mother liquor from which the hydrochloride of alkaloid F36 had been crystallized was basified with ammonia, and the liberated bases were extracted with a large volume of ether. Evaporation of the extract yielded a resinous residue, which crystallized in contact with methanol. The base was dissolved in chloroform and the solution evaporated to a thin syrup. The addition of methanol yielded fine silky needles which melted at  $217^{\circ}\text{C}$ . When recrystallized again in the same manner the *dl*-tetrahydro-coptisine melted at  $222$  to  $223^{\circ}\text{C}$ . and yielded with sulphuric acid a colorless solution which, on heating, only turned brown. The optical activity in chloroform ( $c = 0.4$ ) was  $-5.5^{\circ}$  for the crude base and virtually zero for the purified specimen. The total amount obtained including that recovered from the mother liquor was 0.12 gm. (2.5 p.p.m.). Found: C, 70.20, 70.31; H, 5.31, 5.37; N, 4.64, 4.53%; OMe, negative. Calcd. for  $C_{19}H_{17}O_4N$ : C, 70.59; H, 5.26; N, 4.33%.

#### *Alkaloid F37*

A small amount of this alkaloid was obtained from the mother liquors from which *dl*-tetrahydro-coptisine and alkaloid F36 had been obtained. The greater portion remained in the alkaline filtrate from fraction BC and was obtained from this by ether extraction (fraction EC). It is, however, not phenolic. The residue from the latter, after the removal of the ether, crystallized readily from methanol in which it is moderately soluble. It was obtained in colorless, well defined prisms which melt sharply at  $177^{\circ}\text{C}$ . Dissolved in cold sulphuric acid, it gradually developed a blue color. Gentle heating of the solution greatly intensified the blue color and further heating produces a transient pink which changes to dirty olive. The yield was 1.3 gm. (26 p.p.m.). Found: C, 68.06, 68.32; H, 6.27, 6.23; N, 4.45, 3.72; OMe, 16.62; 16.06%. Calcd. for  $C_{21}H_{23}O_5N$ : C, 68.29; H, 6.23; N, 3.79; 2OMe, 16.80%.

#### *Protopine*

The isolation of protopine from the fraction (BS) has been repeatedly described. It is therefore considered unnecessary to give details except to state that in this case it was purified as the hydrochloride. The base, liberated from the salt and recrystallized, melted at  $210^{\circ}\text{C}$ . and admixture with an

authentic specimen did not lower the melting point. The yield was 24 gm. (0.05%).

#### *Cryptocavine*

The mother liquor from the protopine hydrochloride was basified with potassium hydroxide, and the regenerated bases were converted to hydrobromides in dry methanol. A mixture of salts separated. This was extracted with hot methanol until only the protopine salt remained. The combined extract was evaporated somewhat and on cooling deposited another small crop of protopine hydrobromide. Further evaporation and cooling of the filtrate yielded the not quite pure hydrobromide of *cryptocavine*. It was recrystallized from hot water, from which it first separates as a gelatinous mass which, on gentle warming, changes to a mass of fine needles. The free base regenerated from the hydrobromide was recrystallized from chloroform-methanol. Colorless stout prisms melting sharply at 223° C. were thus obtained. Dissolved in a drop of acetic acid, it yields on the addition of sulphuric acid, a pink solution which gradually becomes blue. Admixture with cryptopine or with corycavine lowered the melting point at least 20° C. However, in admixture with a specimen of cryptocavine from *Corydalis ochotensis* (8) there was no depression in melting point. The alkaloid is optically inactive in chloroform solution ( $c = 0.4$ ). The yield was 1.0 gm. (20 p.p.m.). Found: C, 68.17, 68.38; H, 6.43, 6.57; N, 3.85, 3.90; OMe, 17.37, 16.88, 15.32%. Calcd. for  $C_{21}H_{23}O_5N$ : C, 68.29; H, 6.23; N, 3.79; 2OMe, 16.80%. Calcd. for  $C_{23}H_{25}O_5N$ : C, 68.93; H, 6.53; N, 3.66; 2OMe, 16.19%.

#### *Alkaloid F38*

The fraction (EES) in contact with methanol deposited a sparingly soluble base. This was dissolved in boiling chloroform of which about 800 cc. was necessary. The filtered solution (charcoal) was evaporated to a small volume and crystallization brought to completion by the addition of methanol. The base then melted not quite sharply at 255° C. It was redissolved in hot dioxane in which it is moderately soluble, and the filtered solution evaporated somewhat. The addition of hot methanol induced rapid crystallization of colorless, fine, stout prisms, which melted to a dark tar at 256° C., some shrinking taking place at 240 to 245° C. The yield was about 0.15 gm. (3 p.p.m.). Found: C, 64.46, 64.41; H, 5.38, 5.28; N, 3.88, 3.81; OMe, 8.99, 8.87%. Calcd. for  $C_{20}H_{19}O_6N$ : C, 65.04; H, 5.15; N, 3.79; 1OMe, 8.40%.

#### *Aurotensine*

The mother liquors from which alkaloid F38 had been isolated as well as fraction (BSE) were separately neutralized with hydrogen chloride in small volumes of methanol. Dry ethyl acetate was added until the incipient turbidity just disappeared on mixing. In both cases a small yield of a mixture of hydrochlorides was obtained. They were combined and dissolved in hot water. The rapidly cooled solution was basified with ammonia and extracted with ether. The residue from the ether extract was a mixture. It was

extracted with hot methanol, which left a residue of alkaloid F38 weighing about 20 mg. The methanol extract was evaporated to a small volume and cooled. A mixture of colorless prisms and pink plates separated. The former consisted of F38 and remained undissolved on gentle heating, whereas the pink plates dissolved and recrystallized from the filtered solution. As thus obtained, the bases melted at 128° C. The base was redissolved in hot methanol and the solution evaporated to a small volume. Crystallization was immediately induced by seeding with a crystal of aurotensine and the crystals thus obtained consisted of pale pink, well developed rhombic plates melting at 128° C. Admixture with an authentic specimen of aurotensine did not lower the melting point. The yield was 20 mg. (0.4 p.p.m.).

#### *Isolation of a Neutral Substance*

The fraction (LC) consisted largely of fumaric acid. This was removed by washing the ether solution with aqueous sodium bicarbonate. The dried ether solution was evaporated to a small volume. The residual pale yellow oil deposited a small amount of crystalline material in the course of several days. Adhering oil was largely removed by pressing between layers of filter paper. The crystalline material was recrystallized four times from hot benzene, in which it is moderately soluble. Colorless stout prisms melting sharply at 152° C. were thus obtained. This substance is sparingly soluble in cold benzene and virtually insoluble in hexane. It is insoluble in water but dissolves in hot aqueous potassium hydroxide. Found: C, 67.50, 67.50; H, 8.29, 8.19%. Calcd. for  $C_{11}H_{16}O_3$ : C, 67.35; H, 8.16%. Methoxyl is absent.

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LOBINALINE, AN ALKALOID FROM *LOBELIA CARDINALIS* L.<sup>1</sup>BY RICHARD H. F. MANSKE<sup>2</sup>

## Abstract

*Lobelia cardinalis* L. was found to contain essentially only one alkaloid, which has been named *lobinaline*. Its empirical formula probably is  $C_{28}H_{38}ON_2$ , and this bears no obvious relation to the alkaloids of *L. inflata*. It does, however, yield benzoic acid on oxidation with alkaline permanganate, but only one mono-substituted benzene nucleus is present. Lobinaline mono-hydrochloride is virtually insoluble in cold water but dissolves readily in dilute acids.

The chemical constituents of closely related plant species within a genus frequently display striking similarities. Occasionally an alkaloid is a constituent of all species within a family. More frequently closely related alkaloids are widely distributed in a family, but it is becoming increasingly evident that specific differences are generally accompanied by definite differences in the elaborated alkaloids. Examples are too numerous to quote in detail but such genera as *Lupinus*, *Aconitum*, and *Senecio* may serve as examples, in each of which the alkaloids of different species display an obvious similarity but, as a rule, not complete identity. *Lobelia cardinalis* L., the chemistry of which forms the subject of this paper, contains an alkaloid which bears no obvious relation to the many alkaloids of *L. inflata* L. All of the latter are derivatives of piperidine and contain only one nitrogen atom (2, 3, 4, 5, 6). The main, and perhaps only, alkaloid from *L. cardinalis*, for which the name *lobinaline* is now proposed, contains two nitrogen atoms. Furthermore, it cannot be formed by the condensation of two molecules of an alkaloid from *L. inflata*. The empirical formula,  $C_{28}H_{38}ON_2$ , is not consonant with such a hypothesis. Nevertheless, there appears to be one point of similarity, and that is in the occurrence of a C-benzoyl group (or the corresponding carbinol) in both types of alkaloids, one such group being present in lobinaline.\* It has not been possible to prepare an oxime, although the presence of a ketonic oxygen is still assumed in view of the fact that oxidation with chromic acid results only in deep seated changes. Oxidation with potassium permanganate yields benzoic acid in amount insufficient for the presence of two mono-substituted benzene nuclei.

Further than this, no insight into the constitution of the alkaloid has been obtained. Nevertheless, the properties of the mono-hydrochloride are unique

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\* In a recent study of Eastern North American species of *Lobelia*, Rogers McVaugh (*Rhodora*, 38: 241-263, 1936) has concluded that *L. cardinalis* has probably existed unchanged since Tertiary times. The same may be said for *L. siphilitica* which is the closest relative to *L. cardinalis*. A preliminary examination of the former has shown that lobinaline, however, is definitely absent. One point of similarity of the two species was found in the occurrence of a mixture of resins,  $\alpha$ - and  $\beta$ -viscol, in both plants. Whether or not these substances are characteristic of the genus, remains to be determined. *L. inflata* is regarded as of more recent origin with no certain affinities, but obviously only very distantly related to *L. cardinalis*.

and point to a profound difference between the nature of the two nitrogen atoms. The salt is virtually insoluble in water and its suspension in boiling water yields the insoluble base and the soluble dihydrochloride. The free base, lobinaline, was obtained in crystalline condition only after three to four years of intermittent work and the dihydrochloride has not yet been crystallized.

Dr. Klaus Unna of the Merck Institute of Therapeutic Research, Rahway, N.J., has kindly undertaken to study the pharmacology of lobinaline, and the author takes this opportunity to acknowledge his indebtedness.

The following summary of his findings was submitted by Dr. Unna:

#### LOBINALINE MONO-HYDROCHLORIDE

Lobinaline mono-hydrochloride was tested for its toxicity and its effect on respiration and blood pressure. In all cases the results were compared with those obtained with lobeline sulphate Merck.

The toxicity was determined in mice. Following subcutaneous injection, death occurred first at 800 mg. per kg., whereas the minimal lethal dose for lobeline was found at 300 mg. per kg.

The normal respiration of rabbits and cats—anesthetized with urethane or urethane and chloralose—was not influenced by lobinaline in doses of 0.25 to 3 mg. per kg. intravenously. Even when the respiration had been depressed by intravenous injection of 4 mg. per kg. of morphine hydrochloride, no increase of the rate and depth resulted from the intravenous injection of lobinaline in doses up to 3 mg. per kg.; lobeline, on the other hand, produced marked effects on the respiration in doses of 0.25 to 1 mg. per kg.

Lobinaline was found to depress the blood pressure. The extent of the fall in blood pressure was proportional to the dose administered. It was very slight after 0.25 mg. per kg., but very marked, and in two cases fatal, after 2 mg. per kg. intravenously. The heart rate was unaltered or slightly increased. No symptoms of vagus stimulation were observed. The effect on the blood pressure remained unchanged after atropine. Lobeline on the other hand, caused a fall in blood pressure owing to the very marked stimulation of the vagi. This effect was completely abolished by atropine.

The foregoing data demonstrate that lobinaline is devoid of the characteristic actions of lobeline, that is, stimulation of the respiratory, vasomotor, and vagus centres. It depresses the blood pressure markedly, but in contrast to the effect of lobeline this fall remains unchanged after atropine. In mice lobinaline is less toxic than lobeline.

#### Experimental

The plant, *Lobelia cardinalis*, commonly known as the cardinal flower, was collected during several years as it became available and the alkaloid isolated shortly after drying. From a total of 47.3 kilos there was obtained 180 gm. of crude total alkaloid.

For this purpose the dried and ground material was extracted with methanol and the evaporated extract acidified with hydrochloric acid and diluted with hot water. The remaining methanol was boiled off and the cooled solution filtered through a layer of charcoal. It was then extracted with ether until no appreciable extract was obtained. The solution was then basified with excess ammonia and exhausted again with ether. The crude base obtained from the ether extract consisted of a pale brown viscous resin. Further extraction of the alkaline aqueous solution with chloroform yielded a dark resinous product which, however, was not soluble in dilute acid.

#### *Lobinaline Mono-hydrochloride*

Direct efforts to crystallize the crude alkaloid as well as attempts to obtain crystalline salts proved unavailing. The following procedure, discovered in the course of attempts to separate the total base into fractions of varying



basicity, is direct and yields a pure product. A clarified (charcoal) ether solution of the resinous base is shaken in a separatory funnel with successive portions of dilute hydrochloric acid until crystals make their appearance. At this point the addition of dilute hydrochloric acid is continued until no more solid hydrochloride is obtained. The mixture is filtered and the solid washed alternately with water and with ether. As thus obtained lobinaline mono-hydrochloride is not quite pure. Further purification is effected by shaking with aqueous sodium hydroxide and ether, and repeating the above procedure with the washed ether solution. The air-dried salt is extremely soluble in methanol but does not crystallize satisfactorily when its solution in this solvent is diluted with water, ether, or acetone. It may be recrystallized by dissolving it in chloroform, in which it is moderately soluble, and adding acetone to the somewhat concentrated solution. Fine, colorless needles melting at  $220^{\circ}\text{C}.$ \* are thus obtained. The salt is readily soluble in dilute acids including acetic acid, but is decomposed by boiling with water into the readily soluble dihydrochloride and the resinous base, from both of which the mono-hydrochloride can be regenerated by appropriate treatment. A certain amount of water of crystallization is tenaciously retained and analyses are in best agreement with the sesquihydrate. Found: C, 70.16, 70.19; H, 8.67, 8.72; N, 5.83, 5.78 (Dumas), 5.76, 5.68 (Kjeldahl); Cl, 7.35%. Calcd. for  $\text{C}_{28}\text{H}_{38}\text{ON}_2 \cdot \text{HCl} \cdot 1\frac{1}{2}\text{H}_2\text{O}$ ; C, 69.82; H, 8.73; N, 5.82; Cl, 7.37%.

#### *Lobinaline*

The first crystals of lobinaline were obtained only from the repeatedly purified mono-hydrochloride. When these were available for inoculation the crude mono-hydrochloride sufficed equally well.

The former was dissolved in dilute hydrochloric acid and the solution basified with sodium hydroxide, and the liberated base extracted with ether which had been freed from alcohol and peroxides. The washed solution was dried over potassium carbonate and evaporated to a small volume. Several such solutions were prepared and in one of them a crystal nucleus appeared after several days. Inoculation of the others induced immediate crystallization, which was somewhat hastened by the cautious addition of purified hexane. After washing with ether-hexane the alkaloid was recrystallized from dry ether in which it is moderately soluble. Fine colorless prisms, melting at  $94$  to  $95^{\circ}\text{C}.$  were thus obtained.  $[\alpha]_D^{24} = +22.3^{\circ}$  ( $c = 0.8$  in chloroform). Found: C, 80.79, 80.81; H, 9.02, 9.16; N, 6.62, 6.68%. Calcd. for  $\text{C}_{28}\text{H}_{38}\text{ON}_2$ ; C, 80.38; H, 9.09; N, 6.70%. A methoxyl determination gave 2.36 and 2.26%. This value is much too low for one such group and is probably due to the partial elimination of methyl from an N-methyl group. The mono-hydrochloride was prepared from the purified lobinaline and was identical with the purified salt obtained in the first instance. The various mother liquors were combined and yielded appreciable quantities of the mono-hydrochloride, and it is improbable that alkaloids other than lobinaline will be found in more than traces.

\* All melting points are corrected.

### *Oxidation with Permanganate*

A solution of 1.75 gm. of pure lobinaline in 100 cc. of acetone-water (60 : 40) was treated with finely powdered potassium permanganate (10.1 gm.) until the pink color remained for two hours. The mixture was then diluted with much water and the acetone boiled off. A stream of sulphur dioxide was passed in to dissolve the precipitated manganese dioxide, and then a slight excess of hydrochloric acid was introduced to liberate most of the combined sulphur dioxide. An amorphous precipitate was filtered off and the filtrate repeatedly exhausted with ether, the recovered solvent being used for each successive extraction. The residue from the ether was freed of acetic acid and moisture *in vacuo* at room temperature, and then repeatedly extracted with purified hexane-ether (70 : 30). This treatment decreased the weight of the residue by 0.296 gm., and the extract after evaporation and drying weighed 0.289 gm. The product was almost pure benzoic acid. It was recrystallized from hexane; it then melted either alone or in admixture with benzoic acid at 121° C. The yield of benzoic acid was only 56% of that required for one mono-substituted phenyl group in the alkaloid. The amorphous by-products are largely soluble in alkali and presumably represent oxidation products, but their further oxidation with permanganate is extremely slow. It is nevertheless unlikely that two phenyl groups are present because the amount of benzoic acid which should then have been produced is 1.022 gm. No special significance is attached to the presence of acetic acid in the oxidation product. It is highly probable that it might have arisen from the oxidation of some of the acetone.

Oxidation with chromic acid in dilute sulphuric acid at steam bath temperatures was slow, and a substantial amount of the lobinaline used was recovered as the mono-hydrochloride.

### *Oxidation with Mercuric Acetate*

The procedure of Gadamer (1) was followed in detail. A solution of the mono-hydrochloride (1.000 gm.) in 5 cc. of acetic acid was treated with a solution of 6 gm. of mercuric acetate in 30 cc. of water containing 1 cc. of acetic acid. A small amount of mercurous acetate was deposited at room temperature in the course of 12 hr. The mixture was then heated for three hours on a steam bath, cooled, and the crystalline precipitate filtered off and washed with a little cold water. After drying to constant weight at 110° C. it weighed 1.6434 gm. The oxidation of four hydrogen atoms requires 2.1664 gm. The yield was therefore 76% of the theoretical on such a supposition.

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## HEAT CAPACITY OF ETHYLENE IN THE CRITICAL RANGE<sup>1</sup>

By D. B. PALL<sup>2</sup> AND O. MAASS<sup>3</sup>

### Abstract

Some of the data of a previous publication on this subject have been experimentally verified. The calorimeter has been improved so as to increase the accuracy of the new results by a factor of four. The ethylene was purified by means of a new still giving very sharp separations. Good agreement between the present results and those found previously is shown.

### Introduction

In a previous paper, values for the heat capacity of ethylene over a range of temperatures near the critical region were reported (1). In particular, it was found that the heat capacity of the system just above the critical temperature is a function of the thermal history. It seemed desirable to check this result with that obtained with a sample of ethylene purified in a different manner, and in an apparatus showing improved accuracy.

#### *The New Calorimeter*

The method inherent in the use of the new calorimeter was, like that of the calorimeter used previously, an adiabatic electrical method for measuring heat capacity at constant volume.

The essential change lay in the use of a new type of container for the ethylene. Instead of a cylindrical steel bomb immersed in a mercury bath, there was used a spherical brass bomb, whose surface was uniformly wound with a single length of wire, which served the purpose of a heating coil (Fig. 1). Thus the temperature everywhere on the surface was the same during heating.

The method of sealing after introduction of the medium was not altered; as before, the new bomb was fitted with a gooseneck into which solder was melted under vacuum, in order to effect closure.

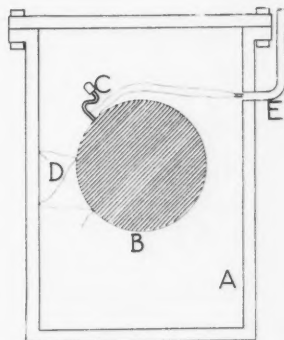


FIG. 1. The calorimeter. A, Steel outer container. B, Spherical brass bomb, whole surface wound with No. 28 copper wire. C, Gooseneck, cutoff after filling and sealing under vacuum. D, Two of the seven thermocouples connected in series. E, Outlet for the bomb-heater leads. There are two other outlets, one for the thermocouple leads, and the other for evacuation of the calorimeter.

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The new bomb was  $2\frac{5}{8}$  in. in diameter; it had a volume of 150 ml. and weighed 115 gm. Uniformly wound with No. 28 enamelled copper wire, the electrical resistance was 18 ohms, and the heat capacity 14 cal. per °C. The ratio of heat capacity to volume was so improved over that of the old container, that heat capacity measurements on ethylene at a density of 0.2255 and a temperature of 10° C. could be made with one-fourth of the previous error.

An additional change made was the conversion of the thermocouples from the radiation to the contact type. Actually, less heat is conducted between the inner and outer parts of the apparatus by contact than by radiation thermels; the amount is in any case negligible in comparison with conduction by air. Seven contact thermels gave a greater sensitivity than twelve radiation thermels.

The manner of operation was the same as that described for the previous apparatus.

### Purification of the Ethylene

An absolute check on the purity of the material used in the new bomb appeared to be desirable. For this reason a low temperature still was constructed, designed after the Podbielniak stills (2), with modifications making it suitable for the purification of large quantities of gases. The still had a vacuum jacketed column 100 cm. long and 3.8 mm. in diameter. Boiling temperatures were measured by means of a copper-constantan thermocouple to better than 1° C. The separations effected by this apparatus are very sharp. The stock was tank material, about 99.7% pure, supplied by the Ohio Chemical Company. Ten per cent first and last fractions were discarded, and no change could be detected in the boiling point of the middle fraction.

### Results

The bomb was so filled that the average density was the same as that used in the previous work, namely 0.2255.

Three sets of data were experimentally determined:

(1) *Dependence of heat capacity of ethylene on the thermal history.* The maximum difference due to extreme variation of thermal history of the heat capacity of the whole system at constant volume between 9.36 and 10.36°C. was found to be 3.1%. The separate results are listed in Table I. In the first paper on this subject (1) the value 2.6% was reported for this same quantity. However, it was thought that there might be an error as great as  $\pm 1\%$  in this figure. The new value of 3.1% is probably good to about 0.3%, so that the existence of this thermal history effect in heat capacity is definitely placed outside of the limit of experimental error.

In the range 9.36° to 10.36° the two fillings give as absolute values of the heat capacity of the heterogeneous system, 0.609<sub>3</sub> and 0.603<sub>2</sub>, again in good agreement.

TABLE I  
DEPENDENCE OF THE HEAT CAPACITY OF ETHYLENE ON THE THERMAL HISTORY.  
9.36 TO 10.36° C. AVERAGE DENSITY, 0.2255

Type of system	$C_p$ , cal./°C./gm.	Mean $C_p$ , cal./°C./gm.
Heterogeneous (brought to initial temp. from below 8° C.)	0.6040 0.6040 0.6017	0.6032
Homogeneous (brought to initial temp. from above 13° C.)	0.5846 0.5818 0.5866	0.5843

(2) *Heat capacities below the critical temperature (Table II).* In this case, the absolute agreement with the previous results is not as good. However, the position of the maximum in the heat capacity curve at 9.0° C. is verified, and the same sharp drop between 9.2° C. and 9.4° C. is noted. The results are listed in Table II.

TABLE II  
HEAT CAPACITY OF THE SYSTEM ETHYLENE BELOW THE CRITICAL TEMPERATURE  
AVERAGE DENSITY, 0.2255

Range, °C.	8.72-8.84	8.84-9.01	9.01-9.21	9.21-9.35
Average heat capacity, cal./°C./gm.	1.483	1.529	1.524	0.993

(3) *Time lag results.* These appear in Table III. The mathematical background of the functions used is described in the article on the previous part of this work (1). Owing to the great change in the ratio of the heat capacity of ethylene to the heat capacity of the container, comparison of these results

TABLE III  
UNIMOLECULAR RATES, AND  $\Delta T_0$  VALUES, FOR TIME LAGS

Range, °C.	Temperature interval, °C.	Time of heating, sec.	$\Delta T_0 \times 10^3$ , °C.	$\Delta T_0 \times 10^3$ , corrected to a 0.2° range	$k$ , sec. <sup>-1</sup> $\times 10^4$
8.72 - 8.84	0.122	550	82	134	5.1
8.84 - 9.01	0.172	800	109	127	3.55
9.01 - 9.21	0.196	910	118	120	1.75
9.21 - 9.35	0.142	475	41.5	58	1.9

with those previously obtained is difficult. However, at least approximate agreement can be demonstrated. At 8.84° C.,  $k$  for the first bomb is  $6.1 \times 10^{-4}$  sec.<sup>-1</sup>; for the second it is  $5.1 \times 10^{-4}$  sec.<sup>-1</sup>. Similarly the results for the heat absorbed after heating through the interval 9.01° to 9.21° C. are

respectively 0.14 and 0.23 cal. per gm., corresponding to the widely different  $\Delta T_0$  values of 0.029° C. and 0.120° C.

In this same region no time lags were observed on lowering the temperature through an interval.

### Conclusions

It may be stated that there is good agreement between these results and those obtained previously (1) with a different gas sample and a different apparatus. The new apparatus appears to function in a very satisfactory manner. The smaller limit of error places the difference in heat capacity due to thermal history definitely beyond the limit of experimental error. Thus the theoretical conclusions drawn in the previous work are placed on a more solid experimental groundwork.

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## AN INVESTIGATION OF THE HYDROGEN-CHLORIDE-PROPYLENE REACTION IN THE REGION OF THE CRITICAL TEMPERATURE<sup>1</sup>

BY C. H. HOLDER<sup>2</sup> AND O. MAASS<sup>3</sup>

### Abstract

The reaction between hydrogen chloride and propylene has been studied in the gaseous state above the critical temperature and in the liquid state just below the critical temperature. Pressures were used such that the density of the gaseous mixtures could be made as great as the density of the liquid mixture at some temperature.

The rate of reaction above the critical temperature increases slowly with increasing pressure until a certain critical density is attained, after which the rate increases rapidly. In the liquid state the reaction has a positive temperature coefficient except for a 25° temperature range just below the critical temperature. In this region there is a rapid decrease in density of the medium with rise in temperature and a negative temperature coefficient occurs.

The density of the liquid reactants at a number of temperatures just below the critical temperature (here defined as the temperature where the visible meniscus disappears) has been reproduced above the critical temperature for a small temperature range. The reaction velocity data obtained under these conditions show a minimum in passing through the critical temperature region.

The above results have been interpreted on the basis of a "structure" characteristic of the liquid state which favors higher reaction velocity and which may exist above the critical temperature at sufficiently high densities.

### Introduction

A survey of the literature has revealed very few reaction velocity measurements in the liquid phase which can be compared to the rate in the gaseous phase. This is not surprising in view of the experimental difficulties involved and the necessity of obtaining a set of reactants that must meet a number of requirements.

Trautz (11, 12) studied the reaction between nitric oxide and chlorine and report that it takes place via the intermediate compound  $\text{NOCl}_2$ . The value for the termolecular constant in the liquid phase at  $-58^\circ$  is 10 (gram molecules per litre)<sup>-2</sup> sec. <sup>-1</sup> as compared with the corresponding value of 0.7 found by extrapolation of the data for the gaseous system. In the condensed state, therefore, the rate is about 14 times as fast as that in the gaseous state.

The racemization of pinene has been studied in the gas phase at low pressure and in the liquid phase, where the concentration is 1000 times greater (7). The reaction is homogeneous and monomolecular at both concentrations, so that in both phases the rate constant is virtually the same.

The object of the present work was to ascertain whether there is a property of the liquid state other than concentration that is responsible for chemical reaction, and whether this property manifests itself in a negative temperature

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coefficient for reaction velocity measurements as the system passes through the critical temperature from the liquid to the gaseous states at equal density. It has been suggested that the temperature coefficient is governed not solely by activation phenomena but also by the destruction, with rise in temperature, of orientated groups of molecules within the body of the liquid. The view has been taken that the liquid state is characterized by a "dynamic structure" due to the formation of these groups. Increase in concentration and lowering of temperature tends to promote the formation of "dynamic structure". Increase in concentration has the more marked influence particularly when a "critical concentration" is passed. Thus "structure" formation is possible above the so-called critical temperature provided the concentration is above a "critical concentration". If the presence of a "structure" promotes the velocity of a chemical reaction the rate of reaction will diminish above the critical temperature if this is the temperature at which the liquid "structure" is destroyed.

The reaction between propylene and hydrogen chloride has been studied previously in this laboratory by Sutherland and Maass (8). They found that the reaction rate above the critical temperature falls off to a value that is virtually zero. The present authors have found it necessary to use gaseous mixtures of a somewhat greater density as a basis of comparison with rates of reaction in the liquid mixtures, and that under such conditions the reaction does take place in the gaseous state to a greater extent than was expected from the conclusions of Sutherland and Maass.

### Experimental

The apparatus is essentially the same as that used by Sutherland and Maass (8) and later described by Holder and Maass (4).

In view of the results obtained in a study of the effect of small amounts of water on the reaction in the liquid state (1), great care was taken to have the gases free from all impurities, especially water vapor. A distillation of a sample of propylene in a Podbielniak column showed that the fraction used was a pure product.

Propylene and hydrogen chloride were prepared as described by Maass and co-workers (2, 6).

### Results

#### *Propylene-hydrogen-chloride system*

It was desired in this research to compare the rate of reaction in the liquid state with that in the gaseous state at the same density. An ideal system for such an investigation must meet a number of requirements. The critical temperatures of both the reactants and the reaction products should be within a fairly narrow temperature range so that condensation will not take place at the higher pressures. The compressibility of the mixture should be such that densities equal to those in the liquid state may be obtained at pressures that do not involve too great a risk to the experimenter. The hydrogen-chloride-propylene system fulfils most of these requirements. The

critical temperatures of the reactants are in a convenient temperature range ( $52^\circ$  and  $92^\circ \text{C.}$ ). However, the critical temperature of the main reaction product, isopropyl chloride, is probably quite high, judging by analogy with the critical temperature of normal propyl chloride, which has a boiling point of  $46.5^\circ$  and a critical temperature of  $230^\circ$  (b.p. of isopropyl chloride is  $36.5^\circ$ ). Consequently, for runs at high pressures there will be a tendency for condensation to take place during the reaction owing to the increase of the critical temperature of the mixture above the temperature of the experiment. The compressibility of a  $2\text{HCl} : 1\text{C}_3\text{H}_6$  mixture is such that densities equivalent to those in the liquid state may be obtained from  $70^\circ$  (critical temperature of the mixture) up to  $100^\circ$ . For a  $1\text{HCl} : 1\text{C}_3\text{H}_6$  mixture, liquid densities may be obtained from  $75^\circ$  (critical temperature of the mixture) up to  $105^\circ$ . Both systems have been investigated. Owing to the catalytic effect of the excess hydrogen chloride (5) the reaction that occurs in the 2 : 1 mixture does so to an easily measurable extent in a few hours, and for this reason this system has been investigated most thoroughly.

It is well to note in passing that the term "critical temperature" when applied to two-component systems does not have the same meaning as for a pure substance (13, p. 269). In fact the term critical region is more appropriate in reference to a mixture of two substances. This is the temperature region from the "plait-point temperature" to the "critical temperature of contact". It is in this region that retrograde condensation occurs. The term critical temperature as used in this paper is the highest temperature at which a liquid phase was present at a pressure somewhat greater than the critical pressure, as observed by Sutherland and Maass (8).

#### *Homogeneity or Heterogeneity of the Propylene-hydrogen-chloride Reaction*

When a mixture of hydrogen chloride and propylene in the molecular ratio 2 : 1 is compressed at 100 atm. and  $105^\circ$  a reaction rate of 0.40 to 0.45% per hr. has been observed, and this can be detected with an accuracy of about 15% for a run of five hours using a reaction cell having a capacity of 0.35 cc. For runs at slightly lower pressures or for shorter periods the rate is less than the experimental error, and it therefore may be considered a zero reaction. This zero reaction for hydrogen chloride and propylene above the critical temperature has been previously observed in this laboratory (8), and was found to hold true even for a 10 hr. run under the above conditions. The writers, on the contrary, have found repeatedly a slow reaction of the order of magnitude indicated above.

The initial runs in new reaction bulbs have been found to vary in such a way as to indicate that the reaction is at least partially heterogeneous, since it appears to depend on the condition of the glass walls of the individual reaction bulb. A large number of runs were made in order to investigate this behavior. The conclusions arrived at may be explained however by considering a few typical cases.

The reaction cells were blown from heavy wall Pyrex tubing (1 cm. internal diameter, 3 mm. wall). Eleven of these, which ranged in capacity from 0.170



to 0.414 cc., were used. For convenience of comparison, in these experiments on catalysis, runs were always made at 105° C., 100 atm. pressure and density 0.265. Under such conditions most of these reaction cells gave an initial rate of the order of 3.5% per hour for the first run. On the other hand, four cells were used which gave initial rates of 0.50, 0.30, 0.35, 0.68% (average of 0.45%) per hour for the first run. The former are then about eight times as fast as the latter. The initial rate in "fast" cells was not a steady state, as shown by subsequent runs. In such cases the rate invariably decreased. It was at first found that the reactions in all "fast" bulbs after a number of runs came to a steady state that was of the same order of magnitude as that in the originally "slow" bulbs. However a number of cells have since been prepared which reach a steady state at twice this rate. In one case runs were made that gave a total reaction time of 215 hr. but this failed to reduce the rate below 1.0% per hour.

The effect of reheating the bulb till molten and blowing a partially conditioned bulb is interesting. In such cases the activity is partly but not fully restored. This behavior indicates that the high initial runs in new bulbs cannot be explained fully as due to the presence of moisture which might be present from the operation of sealing in the bulb. It is suggested that the large variation of the activity of the reaction cells, out of all proportion to their variation in size, may be explained on the basis of Taylor's theory (9, 10) of heterogeneous catalysis due to active centres. The existence of "fast" bulbs is due to a large number of active centres on a cell wall, possibly in the form of humps or projections, and vice versa. It is possible that in subsequent reactions these active spots lose their activity owing to an accumulation of reaction products as an adsorbed layer. Thus, on reheating and blowing the walls of such a conditioned bulb the fresh surface will reappear, but the new surface will now be smoother and have fewer active centres, so that the reaction rate is not as high as the original rate.

Since this catalysis found in new reaction bulbs appeared to be due to a condition of the wall rather than to the presence of moisture, it was decided to investigate whether changing the surface area in a bulb that had reached a steady state would increase the amount of reaction in proportion to the increase in surface. As it was desired to avoid the heterogeneous reaction in the experiments to be undertaken later on, this investigation was made with a bulb that had reached a steady state of low reaction rate.

The method employed was to use a reaction cell unit in which the cell proper was spheroidal in shape and was joined at the lower extremity to about 3 cm. of 1.4 mm. bore capillary tubing. The diameter of this capillary was determined by calibration with mercury. The length of the tube occupied by the gases was measured by means of a glass millimetre scale placed behind the tube. From the geometry of spheroids and cylinders it is obvious that allowing the gases to react in one case in the spheroid and in the next case in the spheroid plus about 2 cm. of the cylindrical section introduces an increase in surface per unit volume.

The cell used in these determinations had a volume of 0.171 cc., and if one assumes it to be a sphere the surface area was 1.45 sq. cm. A 2 cm. length of the capillary had a volume of 0.031 cc. and a surface area of 0.88 sq. cm. Thus the change in surface per unit volume when 2 cm. of capillary is exposed is an increase of 35% over that for the spheroid alone.

Measurements were made at 105° and 75° C. and are presented in Table I. The time of reaction was in each case made sufficiently long that an increase in rate proportional to the increase in surface would easily be made evident.

From the results of Table I it is obvious that the small variations in the rates are within the limit of experimental accuracy, and therefore it may be concluded that if a heterogeneous reaction that is proportional to the surface area does occur, then the proportion of the heterogeneous reaction to the homogeneous reaction must be such that an increase of 38% in the heterogeneous reaction gives less than 0.5% reaction (as this amount would have been easily measurable). It follows then that the maximum that can be allotted to the heterogeneous reaction is 19% of the total reaction under these conditions.

On the other hand, it does seem probable that a certain heterogeneity of reaction is present even in these "slow" cells. As mentioned above, all the reaction cells used did not in their steady state exhibit the same rate of reaction. An examination of the rates and relative sizes of the cells readily showed that no relation existed between rate and surface area (a large cell would of course possess a smaller surface per unit volume than a small one). Rather, the speed of a particular cell appeared to be a unique property of that cell. For example, a bulb with a volume of 0.414 cc. gave a rate almost 60% greater than a bulb of 0.171 cc.

It has been found that with bulbs which varied in speed measurably under the conditions of comparison, the results at densities of 0.32 or greater gave rates in very close agreement. Hence, although a small amount of heterogeneous reaction may occur in "slow" bulbs at low densities, this effect is so small a part of the total reaction at high densities that it may be neglected.

Mercury was shown to affect the reaction to a very slight extent. The effect was examined by exposing increasing amounts of mercury surface to

TABLE I  
EFFECT OF SURFACE ON THE RATE OF REACTION IN  
A CONDITIONED BULB

	Run no.	Surface	Reaction, %
105° C. 10 hr. Dens., 265	187	Bulb only	7.0
	188	Bulb only	7.5 Av. 7.2%
	183	38% increase	6.8
	189	38% increase	7.5
	170	23% increase	7.1 Av. 7.1%
75° C. 4 hr. Dens., 352	Curve	Bulb only	7.5
	162	30% increase	7.2
75° C. 4 hr. Dens., 294	165	Bulb only	6.8
	166	30% increase	6.8

the reactants. An estimated increase of surface of 32 times gave an increase in rate from 1.64 to 2.65% in four hours.

*Reaction Velocity of Propylene-hydrogen-chloride above the Critical Temperature*

The data recorded in the following pages were obtained with conditioned cells that gave reaction rates of about 0.50% per hour at 105° C. with the reaction mixture under a pressure of 100 atm. In one case, 91 runs were made in a single cell, and a test run after this time indicated that the cell had been in an equilibrium condition during this period.

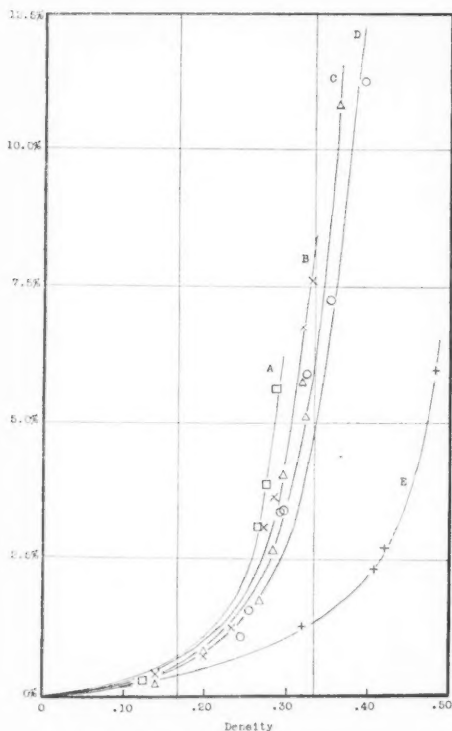


FIG. 1. Isotherms showing percentage reaction in four hours plotted against density. A.  $2\text{HCl} : 1\text{C}_3\text{H}_6$  at 105°. B.  $2\text{HCl} : 1\text{C}_3\text{H}_6$  at 95°. C.  $2\text{HCl} : 1\text{C}_3\text{H}_6$  at 85°. D.  $2\text{HCl} : 1\text{C}_3\text{H}_6$  at 75°. E.  $\text{HCl} : 1\text{C}_3\text{H}_6$  at 85° C.

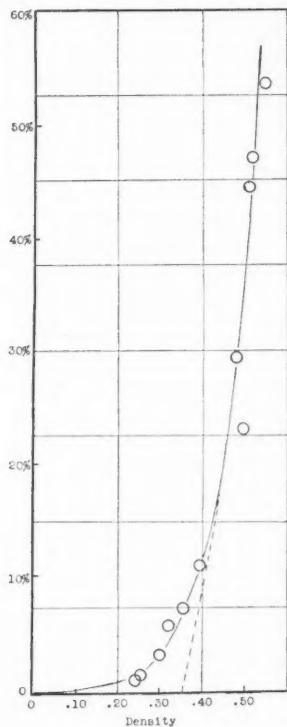


FIG. 2. Isothermal at 75° showing percentage reaction in four hours plotted against density.

The reaction in the gaseous phase has been studied over a wide density range and at temperatures of 75°, 85°, 95°, and 105° C. for a 2 : 1 mixture, and at 85° for a 1 : 1 mixture. These data are tabulated in Table II and are shown graphically in Figs. 1 and 2. The density measurements have been

corrected for a small dead space in the apparatus and for the thermal coefficient of expansion of the reaction cell (Pyrex). The pressure coefficient of expansion has been estimated and found to be negligible. The density of the reactants was measured during each reaction velocity determination as described by Holder and Maass (4). The amount of reaction is expressed, for comparison, in terms of a four hour run, but in practice the time chosen was that which would give sufficient reaction to be easily measurable, but not long enough for large amounts of reaction product to form. This assumption, that the reaction is linear with time, has been found to be true for a temperature of  $105^\circ$ , and from the curve for  $75^\circ$  in Fig. 6 it is seen to be true for rates of reaction up to about 15%. A curve showing the rate of reaction with increasing density for a  $1\text{HCl} : 1\text{C}_3\text{H}_6$  system at a temperature of  $85^\circ$  has been included. In view of what has already been said in regard to the formation of a reaction product with a high critical temperature, it is

TABLE II  
RATE OF PROPYLENE-HYDROGEN-CHLORIDE REACTION ABOVE THE CRITICAL TEMPERATURE

Reaction Cell No. 7B			Reaction Cell No. 10B		
Run No.	Density	Per cent reaction in 4 hours	Run No.	Density	Per cent reaction in 4 hours
$105^\circ$			$85^\circ$ (cont'd)		
111	0.125	.28	155	0.316	5.7
112	.203	.74	154	.361	10.8
113	.264	3.1	153	.445	22.3
114	.273	3.9	222	.491	33.5
115	.287	5.6	232	.542	60.9
$95^\circ$			$75^\circ$		
104	0.138	.42	163	0.241	1.1
99	.199	.74	167	.254	1.6
102	.233	1.3	165	.294	3.4
116	.271	3.1	156	.321	5.9
117	.285	3.6	162	.353	7.2
100	.317	6.7	157	.393	11.2
101	.329	7.6	158	.437	16.5
229	.484	42.5	161	.480	29.4
$85^\circ$			159	.496	23.3
105	0.138	.21	185	.513	44.4
106	.200	.83	160	.520	47.0
107	.266	1.8	233	.544	53.4
108	.286	2.7	$1\text{HCl} : 1\text{C}_3\text{H}_6, 85^\circ$		
110	.294	4.1	207	0.318	1.3
109	.315	5.1	208	.408	2.4
			220	.422	2.7
			209	.485	6.0

very likely that the reactions at 75° at high densities are accompanied by the formation of a liquid phase as the reaction proceeds.

The curves of Figs 1 and 2 show a number of interesting features. The curve for 75°, Fig. 1, which is just 5° above the critical temperature, rises very slowly at first until a density of about 0.27 is reached, at which the slope increases more rapidly. At higher densities the curve becomes very nearly a straight line. If this portion of the curve is extrapolated to zero reaction we find that it cuts the density ordinate at about 0.35, which,

as shown later, is the value of the critical density of the mixture. The conclusion that arises from such a result then is that the reaction above the critical temperature depends essentially on the attainment of a concentration comparable to that in the liquid state.

If the data at 85° for the 2 : 1 and 1 : 1 mixtures are now plotted as percentage reaction *versus* partial density of hydrogen

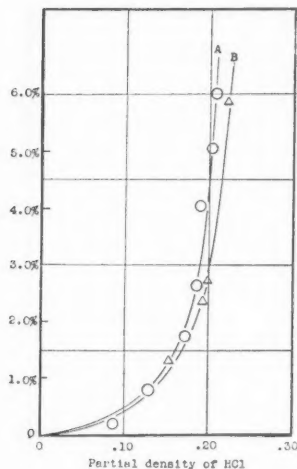


FIG. 3. Percentage reaction in four hours plotted against partial density of hydrogen chloride for mixtures at 85° C. Curve A is for 2 : 1 mixture. Curve B is for 1 : 1 mixture.

TABLE III  
DENSITY OF LIQUID MIXTURES

Temp., °C.	Density 2 : 1	Density 1 : 1
25	0.675	
35	0.659	
45	0.628	
50	0.600	
60	0.544	0.526
65	0.480	0.510
70	0.350 (calcd.)	0.457
75		0.320 (calcd.)

chloride, as in Fig. 3, it is observed that the two curves are very close together.

#### Measurement of the Density of Liquid Mixtures

The densities of  $2\text{HCl} : 1\text{C}_3\text{H}_6$  mixtures have been measured at temperatures from 25° to 65° C. inclusive, and those for a  $1\text{HCl} : 1\text{C}_3\text{H}_6$  mixture at temperatures from 50° to 70° inclusive. These data are recorded in Table III and shown graphically in Fig. 4. These measurements were made by calculating the mass of reactants (measured out in calibrated volumes) that was necessary to fill completely the reaction cell of known volume with liquid. Each curve has been extended to a density at its critical temperature that is the mean of the critical density of hydrogen chloride and that of propylene. These points fit on curves that can be obtained by extrapolation of the observed densities at lower temperatures.

*Reaction Velocity of Propylene-hydrogen-chloride below the Critical Temperature*

The temperature coefficient of the reaction in the liquid state below the critical temperature has been determined. These runs were made by starting with a cell in which just sufficient pressure had been applied to condense the liquid completely. However, since the reaction takes place with a contraction in volume a vapor phase soon reappears.

Others (5) have found that the reaction has a positive temperature coefficient from  $-78^\circ$  to  $45^\circ \text{C}$ . The writers have investigated the rate from  $25^\circ$  up to the critical temperature. The data are recorded in Table IV and are plotted together with

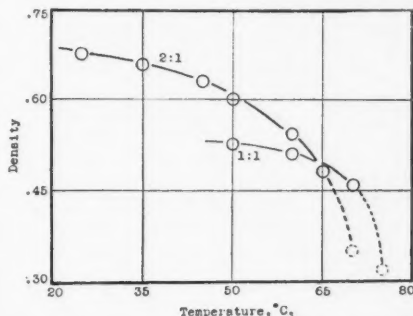


FIG. 4. Density plotted against temperature for 2:1 and 1:1 liquid mixtures.

other data in Fig. 5. The results for both 2:1 and 1:1 mixtures give the same type of curves although the latter are not plotted in Fig. 5. For both mixtures there is a positive temperature coefficient up to about  $45^\circ$ , over which range the density varies only slightly. Between  $45^\circ$  and the critical temperature, through which region the density is changing greatly, the temperature coefficient becomes negative. This will later on be ascribed to a

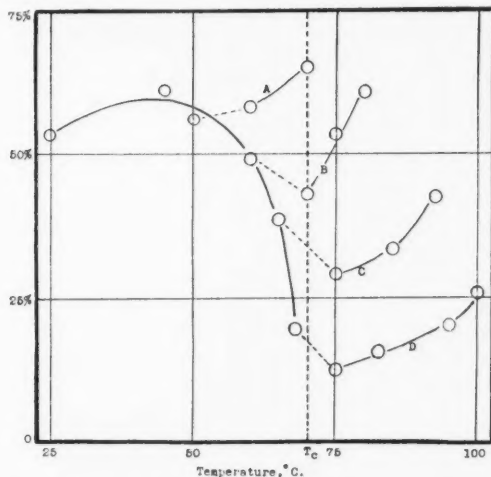


FIG. 5. Percentage reaction in four hours plotted against temperature, showing the negative temperature coefficient in the liquid state and the discontinuity in rate in passing through the  $T_c$  at identical densities.

partial destruction of regional orientation caused by a rapidly diminishing density in this particular temperature range. The probability that this is the cause is made apparent when rates above and below the critical temperature are compared.

TABLE IV  
REACTION IN LIQUID STATE

Temp., °C.	2 : 1 Density	Per cent reaction in 4 hours	Temp., °C.	1 : 1 Density	Per cent reaction in 4 hours
25	0.675	53.6	50	0.526	4.5
45	0.628	61.1	60	0.510	3.6
50	0.600	56.1	70	0.457	3.1
60	0.544	49.2			
65	0.480	39.9			
68	0.404	19.6			

*Comparison of Rates of the Propylene-hydrogen-chloride Reaction for Equal Densities above and below the Critical Temperature*

As the basis of comparison for these experiments, measurements have been made below the critical temperature at a certain temperature with just sufficient pressure to give 100% liquid in the cell at the beginning of the run. The density at this temperature has then been reproduced at a higher temperature by applying sufficient pressure, and the rate has been measured.

TABLE V  
RATE OF PROPYLENE-HYDROGEN-CHLORIDE REACTION  
ABOVE AND BELOW THE CRITICAL TEMPERATURE (70°)

Density	Temperature, °C.	Per cent reaction in 4 hours
0.600 (50°)	50	56.1
	60	58.2
	70	65.3
0.544 (60°)	60	49.2
	70	43.1
	75	53.4
	80	60.9
0.480 (65°)	65	39.9
	75	29.4
	85	33.5
	95	42.6
0.404 (68°)	68	19.6
	75	12.8
	85	15.5
	95	20.0
	100	26.0

The results are given in Table V. The first column is a list of densities of the liquid medium as given in Table IV, and the number in parentheses is the temperature at which the liquid mixture has this density. The second column gives the temperatures at which this density was reproduced, and the third column, the percentage reaction in four hours observed at this temperature and density. These results for the 2 : 1 mixtures have been plotted in Fig. 5. The 1 : 1 mixtures show the same effect but to a less pronounced degree and are not plotted.



The curves *B*, *C*, *D* in Fig. 5 show a definite decrease in reaction velocity in the critical temperature region which it is suggested may be explained by the change in properties of the medium in passing from below to above the critical temperature. The continuous nature of Curve *A*, Fig. 5, seems to justify this explanation. In this case the density at 50° was reproduced at two higher temperatures which are still below the critical. This curve indicates a positive temperature coefficient with no dip in the curve for reactions at constant density. However, when a constant density is maintained through the critical temperature one finds a minimum in the curve. For instance, it is seen from the 0.480 density curve that the rate for 65° is 39.9%, and at 75° this has dropped to 29.4%, a decrease of about 25% of the higher rate.

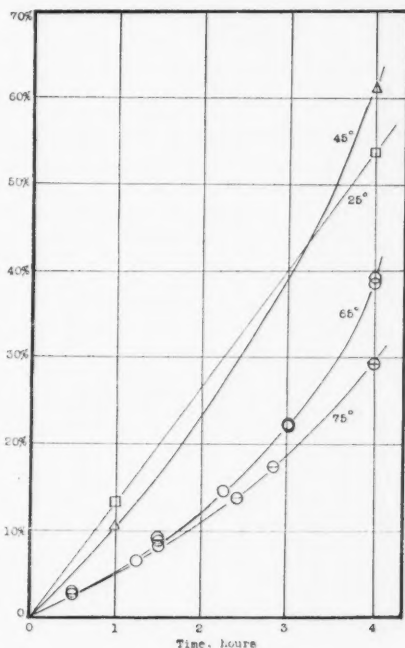


FIG. 6. Percentage reaction plotted against time in hours at 25°, 45°, 65°, and 75° C.

TABLE VI  
RATE vs. TIME DATA AT 25°, 45°, 65°, AND 75° C.

No. of hours	Reaction, %	No. of hours	Reaction, %
65° C., Dens., 0.480		75° C., Dens., 0.480	
0.5	2.9	0.5	2.7
1.25	6.4	1.5	8.8
1.50	9.1	2.42	13.8
1.50	8.1	2.83	17.4
2.25	14.7	4.0	29.4
3.0	22.3	25° C. Dens., 0.675	
3.0	22.2	1.0	13.1
4.0	39.2	4.0	53.6
4.0	38.6	45° C. Dens., 0.628	
		1.0	10.6
		4.0	61.1

It is necessary to raise the temperature to about 93° before the rate at 65° is equaled.

The rate vs. time curve for the reaction at 75°, with a density equal to that of the liquid mixture at 65°, has been plotted in Fig. 6. Similar curves for the reaction in the liquid phase at 25°, 45°, and 65°, starting with 100% liquid phase, are included for comparison. The results are listed in Table VI. The reaction at 25° has been studied extensively by Brown (1), using a somewhat different technique whereby the re-

actants were condensed into heavy walled reaction cells, which were then sealed off at liquid air temperatures. The amount of reaction was followed by titration methods. The results obtained by this method agree very well with those observed by the writers.

The reaction at 25° is linear with time up to four hours, and this has been confirmed by Brown, who made more detailed measurements, whereas those at 45°, 65°, and 75° give rates that increase with time more rapidly than for a linear relation. The contraction of the liquid phase as a reaction proceeds has been observed to be greater for a run at 45° or 65° than at 25°.

If now the rate *vs.* time curves for the reaction at 75° and 65° (above and below the critical temperature respectively) be considered, it will be observed that the curves are close together for the first 1.5 hr., but that after this they separate more and more. When the reaction at 75° has proceeded for about two hours the first appearance of a vapor phase can be noticed. This is attributed to the formation of a reaction product with a high critical temperature in the highly compressed gaseous system. The introduction of this third compound causes the critical temperature of the system to increase, and, when it reaches 75°, liquefaction, as evidenced by meniscus formation at the top, will take place. This would not be observed immediately.

### Discussion

At the time when the rates of reaction between hydrogen chloride and propylene in the liquid state and at low temperatures were first investigated in this laboratory (5), it was observed that no reaction took place in the gaseous state even at relatively high temperatures. A mixture of hydrogen chloride and propylene was kept under observation for a period of a year without any measurable reaction taking place, although this mixture when condensed and sealed off in a bulb reacted to a measurable extent within a few minutes. An experimental technique was then devised for mixing the reactants above the critical temperature and then compressing them to a high degree of density, and the result found was that no measurable reaction occurred until the temperature was lowered below the critical temperature. It was suggested at the time that an explanation might be found in the assumption that the liquid state of aggregation had a "structure", which greatly enhanced the reaction velocity.

A whole series of investigations was then undertaken to determine whether a liquid possessed a "structure" and whether the critical temperature phenomena were due to the rapid disappearance of "structure" in the critical temperature region. Considerable evidence for this was discovered but a slightly different point of view was gradually acquired. Although rise of temperature should undoubtedly tend to destroy "structure", the decrease in density of the liquid in equilibrium with its vapor does the same, and eventually a critical density is approached where a "structure" is destroyed by leaps and bounds. Conversely, a medium at a temperature above its critical temperature and compressed to a pressure greater than its critical pressure such that its

density actually is greater than that of the liquid at its critical temperature should develop a "structure". The investigation of Geddes and Maass (3) seems, particularly, to confirm this conclusion.

With this point of view in mind, the reaction between hydrogen chloride and propylene was reinvestigated, as it was felt that if the foregoing reasoning were correct a liquid "structure" would form even above the critical temperature, provided that the concentration were high enough, and that then if "structure" increases the rate of reaction, measurable rates of reaction should be found even above the critical temperature. In other words, it was expected that an increase in density, once a critical density had been passed, would have a far greater influence on the rate of reaction than increase of temperature in the critical temperature region.

The original apparatus (8) was rebuilt to permit measurements at higher pressures than those used by Sutherland and Maass. Furthermore, since it was realized that densities were the all-important consideration means were devised for more accurate measurements of density than those carried out by the above-named investigators.

It was discovered that in the work of Sutherland and Maass the critical density had not quite been reached, but otherwise their results were in principle confirmed. It was also discovered that the walls of the reaction vessel used by the present writers had a slight catalytic effect which, as was brought out in the discussion of these measurements, was small compared with the measurements of reaction velocity at densities above the critical density. What remains uncertain is whether the catalytic activity can be reduced to an extent such that the reaction velocity is zero at the lower densities.

The critical density at the critical temperature of the  $2\text{HCl} : 1\text{C}_3\text{H}_6$  mixture was estimated to be 0.35. From the results shown in Fig. 1, it is seen that once a density of 0.25 is passed the rate of reaction increases by leaps and bounds with rise in density. In Fig. 2, drawn so as to make possible the inclusion of results at densities where the reaction proceeds up to 55% completion in four hours, it is seen that at  $75^\circ$  the reaction-rate-density relation tends to become linear, and on extrapolation to zero reaction rate gives a density value corresponding to the critical density of the medium at  $5^\circ$  below the temperature of the experiment, namely, the critical temperature of this system.

From Fig. 1 it is also apparent that, as would be expected, activation increases with rise in temperature, for at equal densities the rate of reaction increases. Unfortunately, at the higher temperatures it was not possible to carry out measurements at densities higher than those given because the pressure limit of the equipment had been reached.

In Fig. 1 is shown Curve *E* representing a reaction of a  $1\text{HCl} : 1\text{C}_3\text{H}_6$  mixture at  $85^\circ$ , the same temperature for which data in Curve *C* for a  $2\text{HCl} : 1\text{C}_3\text{H}_6$  mixture were obtained. As mentioned before, plotting both these curves on the basis of the partial density of the hydrogen chloride brings the curves close together. This indicates that for equal concentrations of hydro-

gen chloride, irrespective of the concentration of the propylene, the rate of the reaction is nearly the same. This point is to be investigated further. It is apparent however that the change in rate with hydrogen chloride concentration in no way follows a simple relation. As can be seen from the curve in Fig. 2, in which the abscissae are a measure of the concentration of the

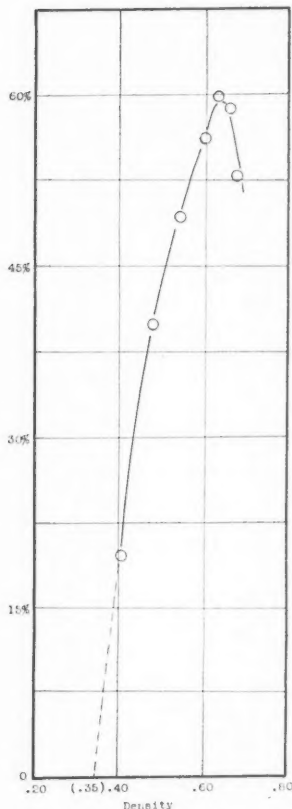


FIG. 7. Density of the liquid medium at various temperatures from 25° to 68° inclusive, plotted against percentage reaction in four hours.

"structure", it may be that at the critical temperature the heat energy of the molecules may reach a critical value where, with further rise in temperature within the neighborhood of the critical density, more rapid destruction of "structure" takes place than at other temperatures. In that case where the concentration is kept constant with rise in temperature, owing to

hydrogen chloride, the rate above a concentration corresponding to a density of 0.4 for the mixture increases approximately according to the 5th power of the concentration of the hydrogen chloride. This shows that the mechanism of the reaction is influenced in the high density region, *i.e.*, the region where presumably the "liquid state" exists, by some factor that does not involve the order of the reaction.

The reason why the rate of the reaction of the liquid mixtures, under pressures corresponding to their vapor pressure, passes through a maximum with change in temperature is now made apparent. As was pointed out before, the rate of the reaction increases with rise in temperature owing to increased activation, but once 45° is passed, the density of the liquid decreases so rapidly (see Fig. 4) that this more than compensates for the influence of increased thermal energy. This is brought out rather well in Fig. 7, in which the percentage reaction for equal times is plotted against density of the liquid, indicating as seen, that at the critical density the reaction rate would be zero. A possible reason why the rate in the compressed gas at densities below this is still appreciable is that a certain amount of "structure" still exists in the highly compressed gas.

The data presented in Fig. 5 give rise to interesting speculations, which the authors, however, at this time do not wish to suggest as other than a tentative explanation. As rise in temperature should tend to destroy the

this effect the rate of reaction is actually decreased and a large increase in temperature is required to bring it back. Thus for curve *A*, where the medium still has a density considerably above the critical density, the temperature coefficient is positive, although it is probably not as large as it would be at lower temperatures. With the mixtures at lower densities the temperature coefficient actually becomes negative. It may be argued that the data are presented for reactions carried out over a four-hour period, and that for a two-hour period the decrease in reaction rate at the critical temperature is less. However, when the time-reaction-rate curves at 65° and 75° in Fig. 6 are examined, it is seen that there is still a negative temperature coefficient at two hours and no indication of a positive temperature coefficient at any shorter time. The ideas advanced concerning the reason for the apparent negative temperature coefficient at the critical temperature are put forward as suggesting further investigation to be undertaken to determine whether they are correct.

From a consideration of the solubility measurements carried out by various workers in the region of the critical temperature, it is felt that an accurate determination of solubility in this region would reveal a curve very similar to that obtained in Fig. 5 for reaction velocity. The expected result is that the solubility found a few degrees above, would be somewhat less than that found a few degrees below, the critical temperature at the critical density. However, at densities greater than the critical density the solubility just above the critical temperature will then be of the same order of magnitude as the solubility in the liquid state at the same density. An apparatus is now being constructed to investigate this problem. The solubility of substances in highly compressed gases is of particular interest to geologists.

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